University of Bath

PHD

The geochemistry of nitrogen species in groundwaters.

Towler, Philippa A.

Award date:
1982

Awarding institution:
University of Bath

Link to publication

Alternative formats
If you require this document in an alternative format, please contact:
openaccess@bath.ac.uk

Copyright of this thesis rests with the author. Access is subject to the above licence, if given. If no licence is specified above, original content in this thesis is licensed under the terms of the Creative Commons Attribution-NonCommercial 4.0 International (CC BY-NC-ND 4.0) Licence (https://creativecommons.org/licenses/by-nc-nd/4.0/). Any third-party copyright material present remains the property of its respective owner(s) and is licensed under its existing terms.

Take down policy
If you consider content within Bath's Research Portal to be in breach of UK law, please contact: openaccess@bath.ac.uk with the details. Your claim will be investigated and, where appropriate, the item will be removed from public view as soon as possible.

Download date: 04. May. 2023

'THE GEOCHEMISTRY OF NITROGEN SPECIES IN GROUNDWATERS'

submitted by PHILIPPA A. TOWLER

for the Degree of Ph.D.

of the University of Bath

1982

COPYRIGHT

"Attention is drawn to the fact that copyright of this thesis rests with its author. This copy of the thesis has been supplied on condition that anyone who consults it is understood to recognise that its copyright rests with its author and that no quotation from the thesis and no information derived from it may be published without the prior written consent of the author.

This thesis may be made available for consultation within the University Library and may be photocopied or lent to other Libraries for the purpose of consultation."

Philippa Towler

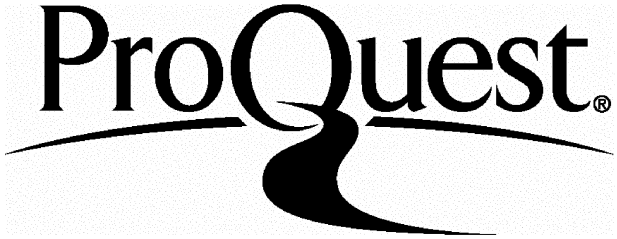
UNIVERSITY OF BATH
LIBRARY
21 28 MAR 1983

ProQuest Number: U334243

All rights reserved

INFORMATION TO ALL USERS
The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript
and there are missing pages, these will be noted. Also, if material had to be removed,
a note will indicate the deletion.



ProQuest U334243

Published by ProQuest LLC(2015). Copyright of the Dissertation is held by the Author.

All rights reserved.
This work is protected against unauthorized copying under Title 17, United States Code.
Microform Edition © ProQuest LLC.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

ABSTRACT

Groundwater NO_3^- concentrations decrease along the hydraulic gradient in the Lincolnshire Limestone ($66mgl^{-1}NO_3^-$) and the Berkshire Chalk ($21mgl^{-1}NO_3^-$) to trace values at the interface between the oxidized and reduced aquifer zone. The NO_3^- is initially diluted by stored pore water, but further down gradient denitrification results in enhanced dissolved N_2 and the appearance of NO_2^-. N_2 is then reduced to NH_4^+ in the deep aquifer.

Semi-quantitative determinations of the N_2/Ar ratio were made by mass spectrometry (±4.9 ratio units, $2\sigma = 2.32$) to detect N_2 gas enhancement by NO_3^- denitrification. $^{15}N/^{14}N$ ratios of nitrogen species were used as provenance indicators and incorporated into a model of the $\delta^{15}N$ of dissolved N_2. Stable Isotope Dilution Analysis, gas chromatography and absolute gas pressure measurements were extensively tested but proved inaccurate in the determination of N_2 concentrations.

In the Lincolnshire Limestone the $\delta^{15}N$ of dissolved NO_3^- (+2.77o/oo and +7.69o/oo ±0.65o/oo) is typical of the soil. The $^{15}N/^{14}N$ ratios for dissolved N_2 shows that it had a lower ^{15}N content than the dissolved NO_3^-. The $^{15}N/^{14}N$ ratios decrease with depth in the aquifer and this is shown to be the result of isotopic fractionation produced by the diffusion of NO_3^- from fissure water into the pore waters and its subsequent bacterial denitrification. NO_3^- reducing bacteria were identified in the Lincolnshire Limestone groundwaters.

Quantitative determination of Ar and other inert gases were used to establish palaeo recharge temperatures and in the Berkshire Chalk the oldest groundwaters were shown to be permafrost meltwater. ^4He and Cl^- concentrations indicated the presence of older groundwaters and the extent of mixing between modern fissure water and stored fluids.

The downdip decrease in NO_3^- concentrations is greater in the Lincolnshire Limestone (4.1 and 1.6mgl^{-1} NO_3^- km^{-1}) than in Berkshire Chalk (0.66mgl^{-1} NO_3^- km^{-1}) where the shape of the NO_3^- concentration profile indicated that contaminated pore waters are present. The continued removal of NO_3^- by dilution with stored pore water is less effective in the Chalk than in the Lincolnshire Limestone.

ACKNOWLEDGEMENTS

I am indebted to the Natural Environment Research Council for financial support throughout the three years of study. The Co-operative Award in the Sciences of the Environment enabled me to use the combined resources of the Institute of Geological Sciences and the University of Bath to complete this thesis. I am most grateful to both organisations.

I wish to thank the members of staff at the Institute of Geological Sciences, the Institute of Hydrology and the members of the teaching staff, postgraduates, the technicians, the glassblowers and the workshop team in Department of Chemistry at the University of Bath for their help, advice and friendship.

To my supervisors, Dr J.N. Andrews of the University of Bath and Dr.W.M. Edmunds of the Institute of Geological Sciences, I extend my profound gratitude for their continued encouragement, inspiration and guidance.

Thank you all for helping me to achieve this ambition.

CONTENTS Page

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

1.1 THE AIM AND SCOPE OF THE STUDY

Increased levels of dissolved nitrate have been observed in groundwaters of the United Kingdom. They are attributed to intensive agricultural practices of high level fertilizer application, the ploughing up of old grassland[1], and improved drainage[2]. Excessive amounts of NO_3^- in potable water are cited as causing methaemoglobinemia in infants, and gastric cancer[3].

The capacity of hydrogeochemical processes and biological denitrification to maintain low concentrations of NO_3^- in these groundwaters has been surpassed. Quantification of these processes is desirable in order to make predictions of future nitrate levels[4]. The passage of nitrogen species through the soil zone is well documented, and the transport of NO_3^- in groundwater has been traced using $^{15}N/^{14}N$ ratios[5]. However, the natural purification processes of the unsaturated zone are not well understood.

In this study the dissolved nitrogen was monitored, by means of the N_2/Ar ratio, to establish the systematic changes between air equilibration and the water table. The effect of gas bubbles entrained in the ground during infiltration on masking nitrogen produced by denitrification of NO_3^- was investigated. An evaluation of the dissolved nitrogen method to elucidate the processes taking place within the unsaturated zone has been made.

The source of the nitrogen gas was investigated by analysis of the $^{15}N/^{14}N$ ratios and related to the ratio of dissolved NO_3^- nitrogen. The influence of isotopic fractionation during the transformation processes of the nitrogen cycle, and the suitability of natural abundance ratio studies to the tracing of nitrogen hydrogeochemistry is discussed.

1.2 NITROGEN

Nitrogen occurs as the triple bonded, diatomic gaseous molecule N_2. It is an odourless, and chemically inactive gas, comprising 78.084 % ±0.004 % of the atmosphere. Atmospheric nitrogen accounts for only 1.96% of the nitrogen in the total earth system (Table 1.1).

Seven isotopes of nitrogen are known (Table 1.2) of which ^{14}N and ^{15}N are stable, and occur in atmospheric nitrogen with a percentage abundance of 99.635 and 0.365[9-11]. This is reflected in natural nitrogen containing substances which have $^{15}N/^{14}N$ ratios of approximately 1:272. Fractionation processes cause slight variations in the natural isotope abundance ratios.

1.3 THE NITROGEN CYCLE

The geochemical cycles interconnect the atmosphere, biosphere, hydrosphere and lithosphere. The nitrogen cycle and hydrological cycle are closely related. Transfer to the inorganic forms of nitrogen through the cycle, and the complex series of microbially governed interconversion processes are dependent on water availability[12].

TABLE 1.1 - THE GEOCHEMICAL DISTRIBUTION OF NITROGEN[8]

	Nitrogen content of the geosphere	
	Kg	%
Atmosphere	4.32×10^{18}	1.96
Lithosphere	2.16×10^{20}	98.03
Biosphere	1.83×10^{14}	0.01

TABLE 1.2 PROPERTIES OF NITROGEN ISOTOPES[13]

ISOTOPE	ATOMIC WEIGHT $^{12}C=12.000000$	HALF-LIFE $t_{\frac{1}{2}}$	MODE OF DECAY	DECAY ENERGIES MeV
$^{12}_{7}N$	12.018900	0.011s	β^+ 100%	17.6
$^{13}_{7}N$	13.005738	9.96 m	β^+	2.22
$^{14}_{7}N$	14.003073	Stable	Isotopes	
$^{15}_{7}N$	15.000108			
$^{16}_{7}N$	16.006089	7.35 s	β^- (α=0.0006%)	10.4
$^{17}_{7}N$	17.008580	4.14 s	β^-, n	8.7
$^{18}_{7}N$	18.014266	0.63 s	β^-	13.9

The nitrogen cycle can be represented as a series of chemical reactions (figure 1.1) linking the various reservoirs of nitrogen (figure 1.2). Five processes transform nitrogen through the cycle:

i) nitrogen immobilization

ii) nitrogen mineralization

iii) nitrification

iv) denitrification

v) nitrogen fixation

Nitrogen in the form of NH_4^+ or NO_3^- is assimilated by micro-organisms and so immobilized. Mineralization of nitrogen releases inorganic forms of nitrogen by microbial degradation or organic nitrogenous compounds such as proteins. During nitrification, the released NH_4^+ is oxidized to NO_3^- by nitrifying bacteria in a two step process

$$NH_4^+ - \text{NITROSOMONAS} \rightarrow NO_2^- - \text{NITROBACTER} \rightarrow NO_3^-$$

Nitrifying bacteria are strictly aerobic requiring high 0_2 concentrations. Nitrobacter is inhibited at pH values above 9.5 in the presence of NH_4^+, leading to the accumulation of NO_2^-. Nitrosomonas is active under alkaline conditions, but is inhibited at pH values below 6.0.

Denitrification occurs in waterlogged soils and in natural water deficient in oxygen. It is necessary that the system is anaerobic. Denitrification involves the microbially catalysed reduction reaction

$$2HNO_3 \rightarrow 2HNO_2 \rightarrow N_2O \rightarrow N_2 \rightarrow 2NO$$

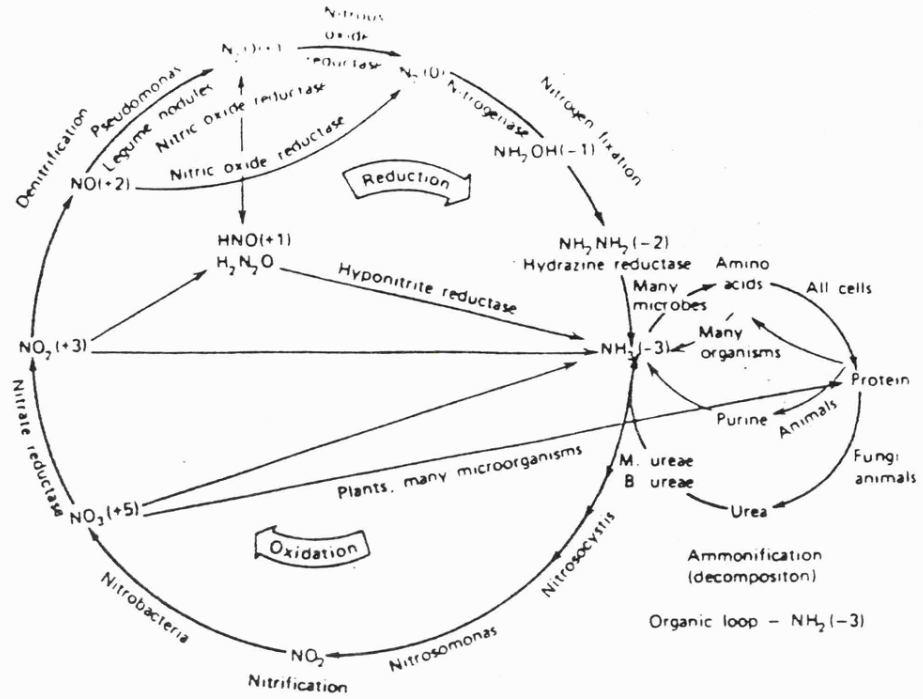


FIGURE 1.1 THE NITROGEN CYCLE[6]

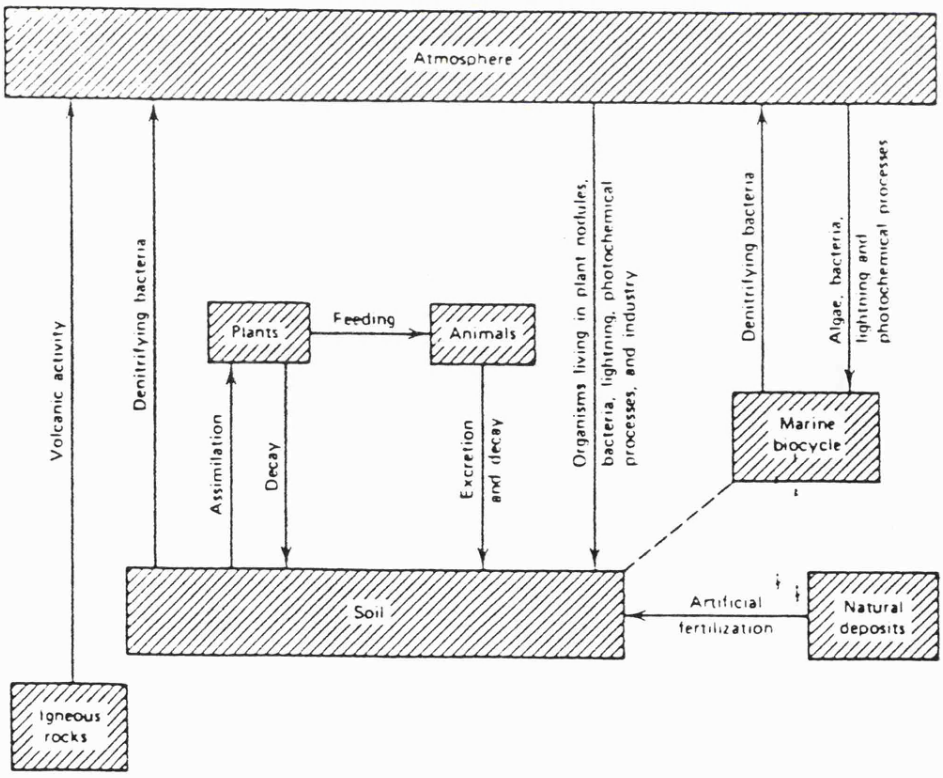


FIGURE 1.2 THE NITROGEN GEOCHEMICAL CYCLE[7]

The most common denitrifying bacteria are Thiobacillus denitrificans, Micrococcus denitrificans, Pseudomonas denitrificans and Achromobacter. Denitrification is inhibited below pH 5.0. Below pH 6.0 nitrogen production is inhibited and NO_2^- is the product. Chemical denitrification may occur by which nitrogen may be lost in gaseous form. Nitrites in a slightly acid solution, in contact with urea, sulphur compounds or carbohydrates will evolve N_2. This reaction is significant after fertilizer application[14].

$$2HNO_2 + CO(HN_2) \rightarrow CO_2 + 3H_2O + 2N_2$$

Nitrogen gas is returned to the cycle from the atmosphere by nitrogen fixation, mediated by bacteria.

1.4 THE NITROGEN CYCLE IN HYDROGEOLOGICAL SYSTEMS

1.4.1 HYDROGEOCHEMICAL PROCESSES

The primary sources of groundwater nitrogen are from precipitation, surface water and the soil. Nitrate in rain varies with locality and season. The range of concentrations overland being 0.3 to 2.5mg/l^{-1} decreasing towards the oceans[15], where 0.15 to 0.5mg/l^{-1} are found[16,23]. An inverse relationship occurs between the amount of precipitation and the concentration of NO_3^- and NH_4^+ [17]. In unpolluted areas the seasonal maximum is found in spring and summer which indicates a source in the soil[18]. Recharge water generally infiltrates through the soil zone and reflects the transformation processes of the nitrogen cycle. In karstic areas, surface water directly enters an aquifer via swallets and is immediately subject to hydrogeochemical processes (figure 1.3).

The processes may be subdivided into physical, chemical and bio-

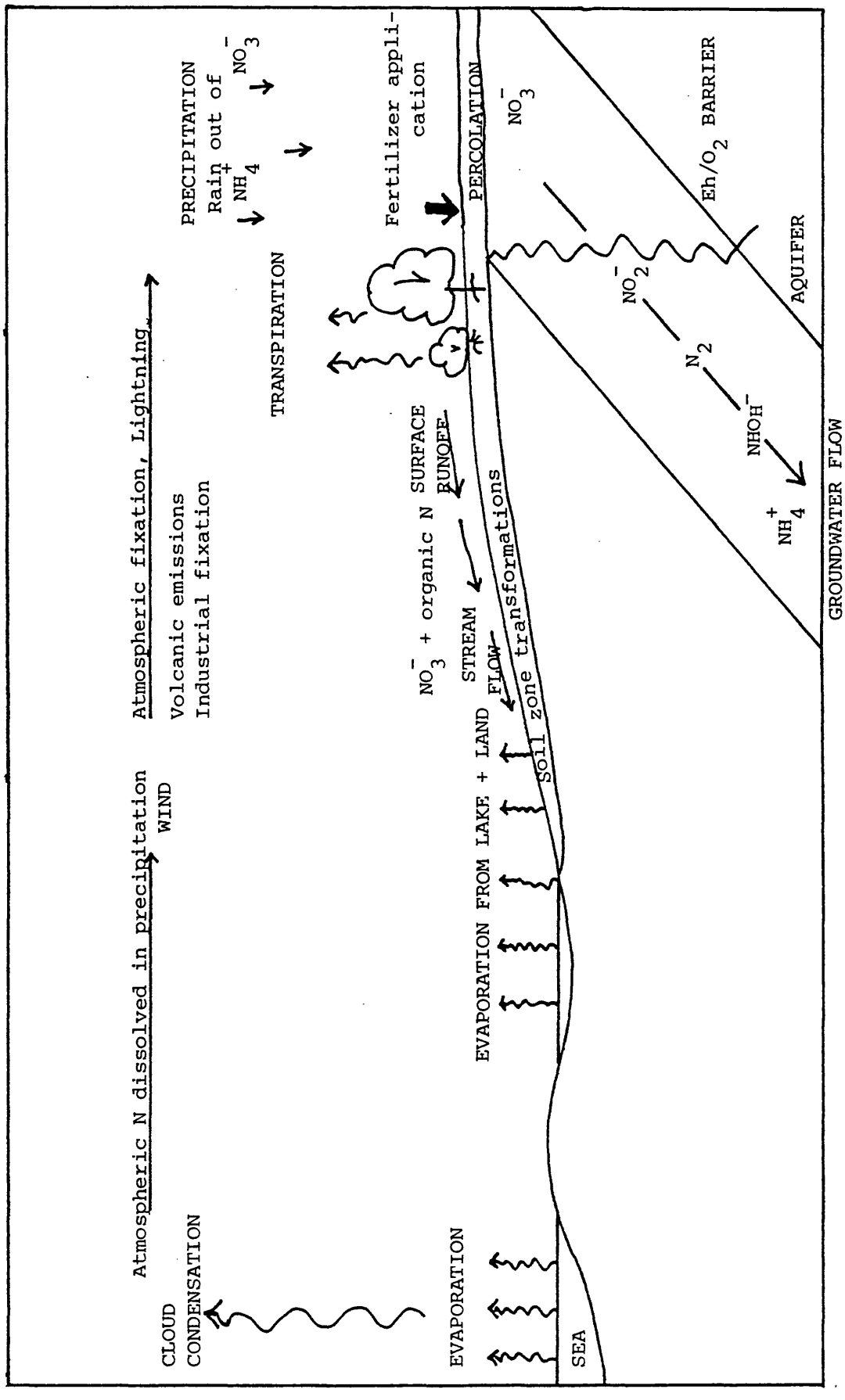


FIGURE 1.3 THE INTERCONNECTED NITROGEN AND WATER CYCLES

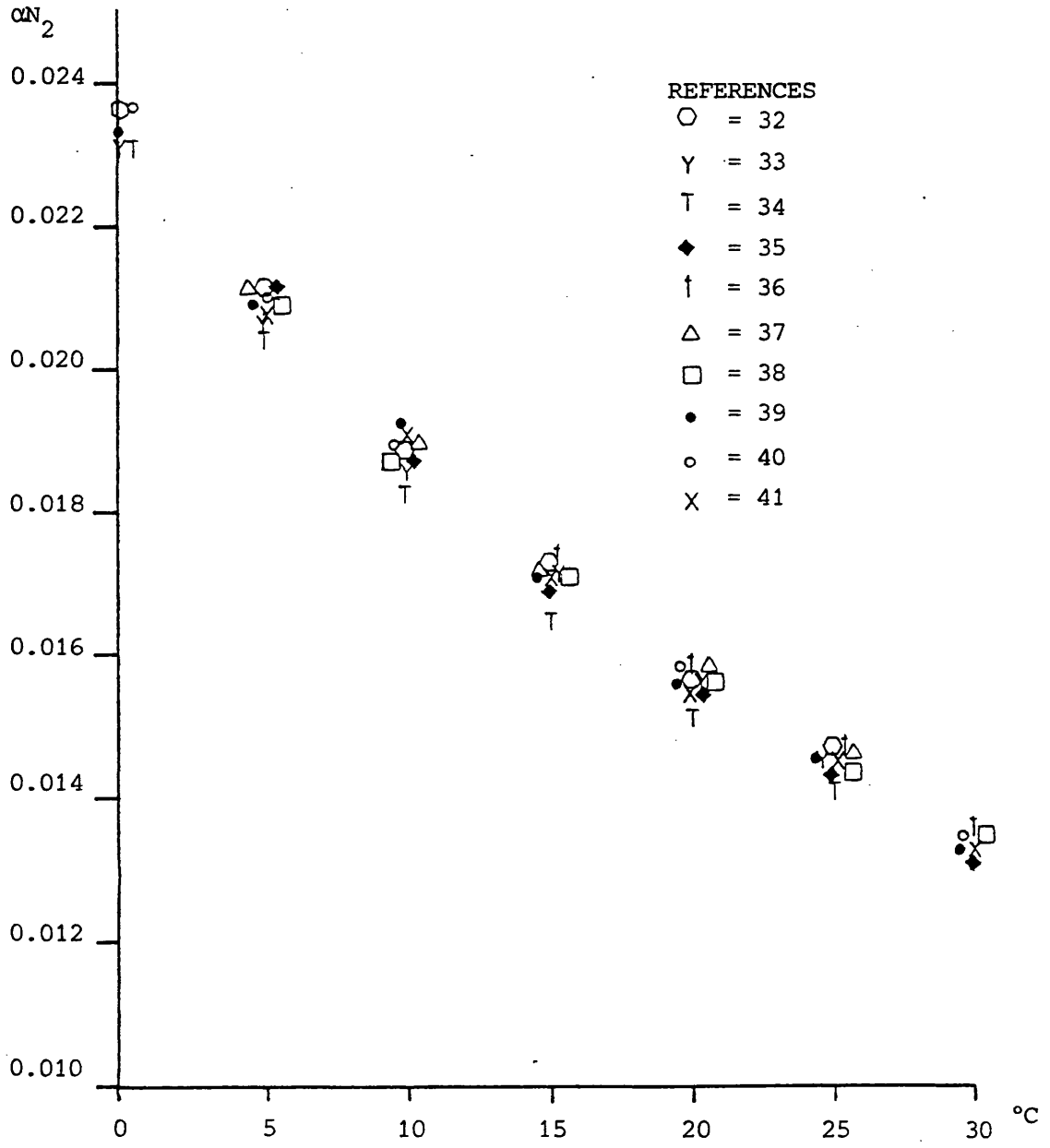
chemical. The physical processes of mixing, dispersion and infiltration are affected by the solute transport mechanisms and the size of particulate matter in relation to the primary and secondary porosity of the aquifer[19].

Solubility is the most important physical property of molecular nitrogen controlling its geochemistry. All other inorganic forms of nitrogen are soluble to a varying extent. Oxidation-reduction reactions govern the stability of these different species occurring in ground waters[20-22]. The contribution from the solid geology to the nitrogen concentration is low since rocks have average nitrogen contents of 47 ppm and 518 ppm for igneous and sedimentary rocks respectively[23]. Only where organic matter, as in clays, or volcanic deposits[24] occur will the geology be significant. The acid-base reactions of ground waters may limit the biochemical nitrogen transformations which are effective over a limited pH range. Denitrification will contribute to raising the pH[19]. The cation, NH_4^+, takes part in ion exchange and surface reactions, and is also affected by the membrane filtration property of clays[25].

1.4.2 NITROGEN SOLUBILITY

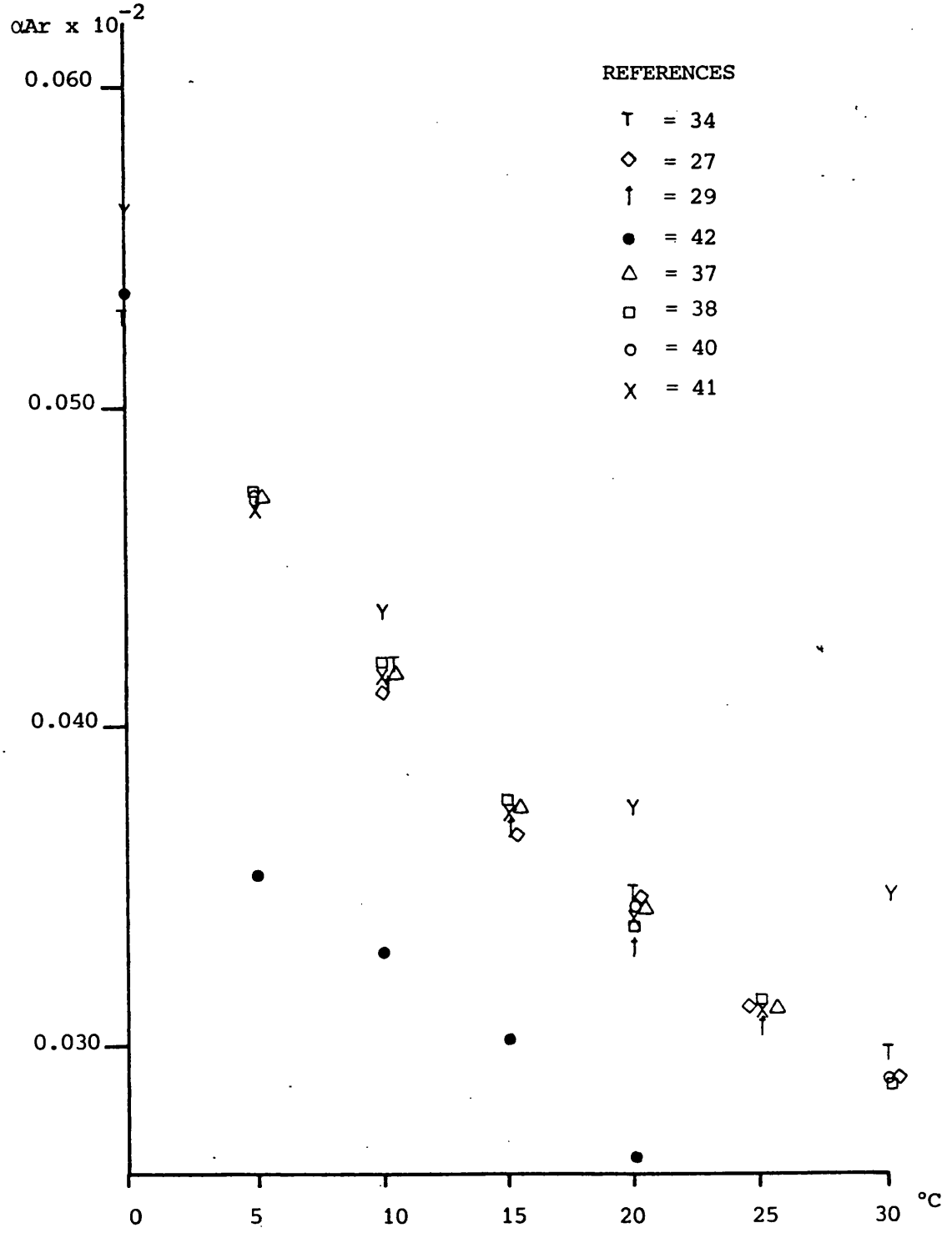
Nitrogen is a conservative gas[26], and is similar in solubility characteristics both to argon and to the other inert gases. Precise measurement of the solubilities of N_2 and Ar in distilled water and seawater by various workers have shown excellent agreement (figures 1.4-1.7)[27-41].

From the measurement of dilute aqueous solutions of seven non-polar gases, including nitrogen and argon, a universal solubility equation



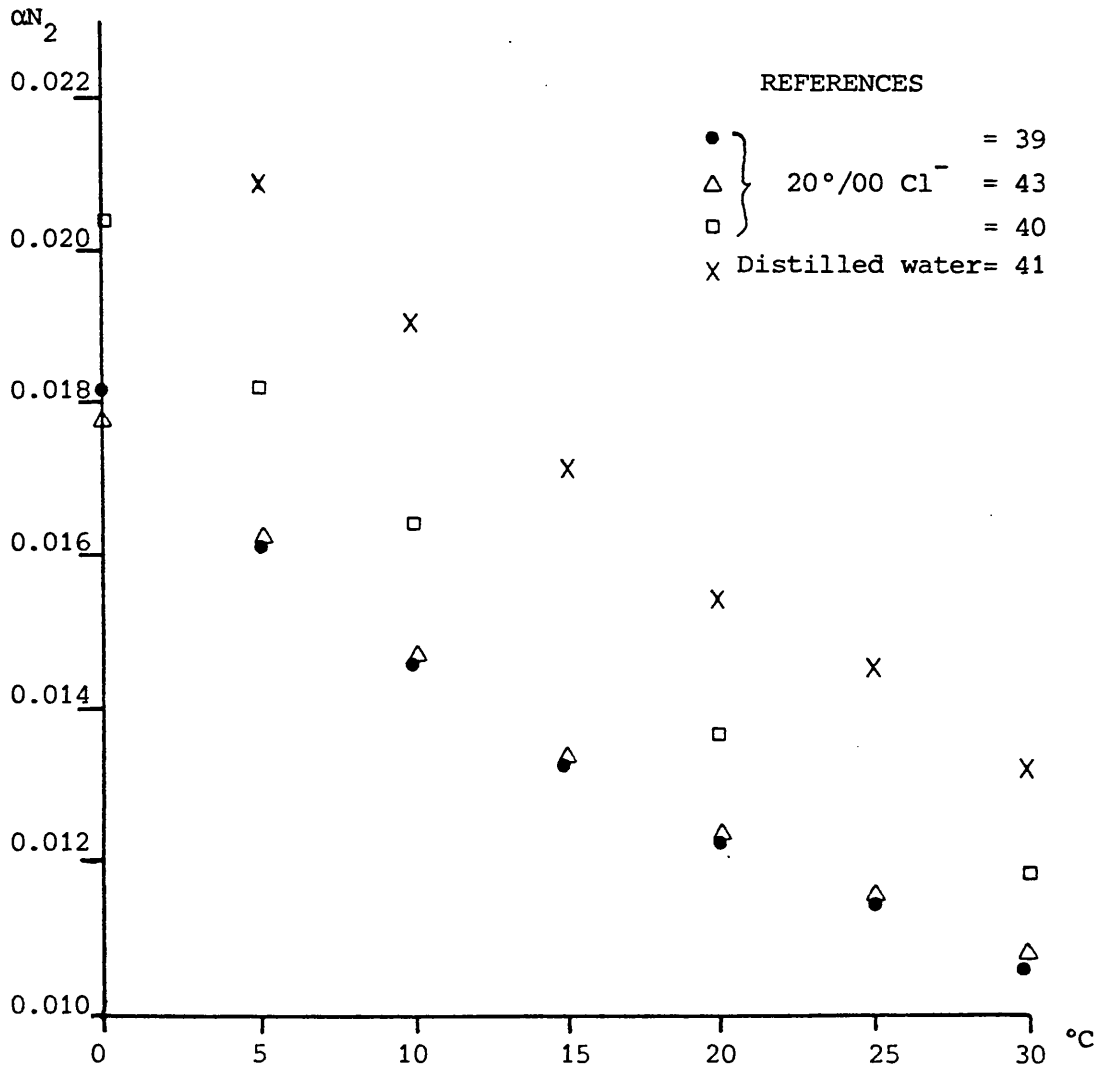
α = the solubility coefficient, the number of cm^3 of gas measured at STP, dissolved in 1l of water in equilibrium with the gas when its partial pressure is 760mm Hg.

FIGURE 1.4 A COMPARISON OF NITROGEN SOLUBILITY DATA



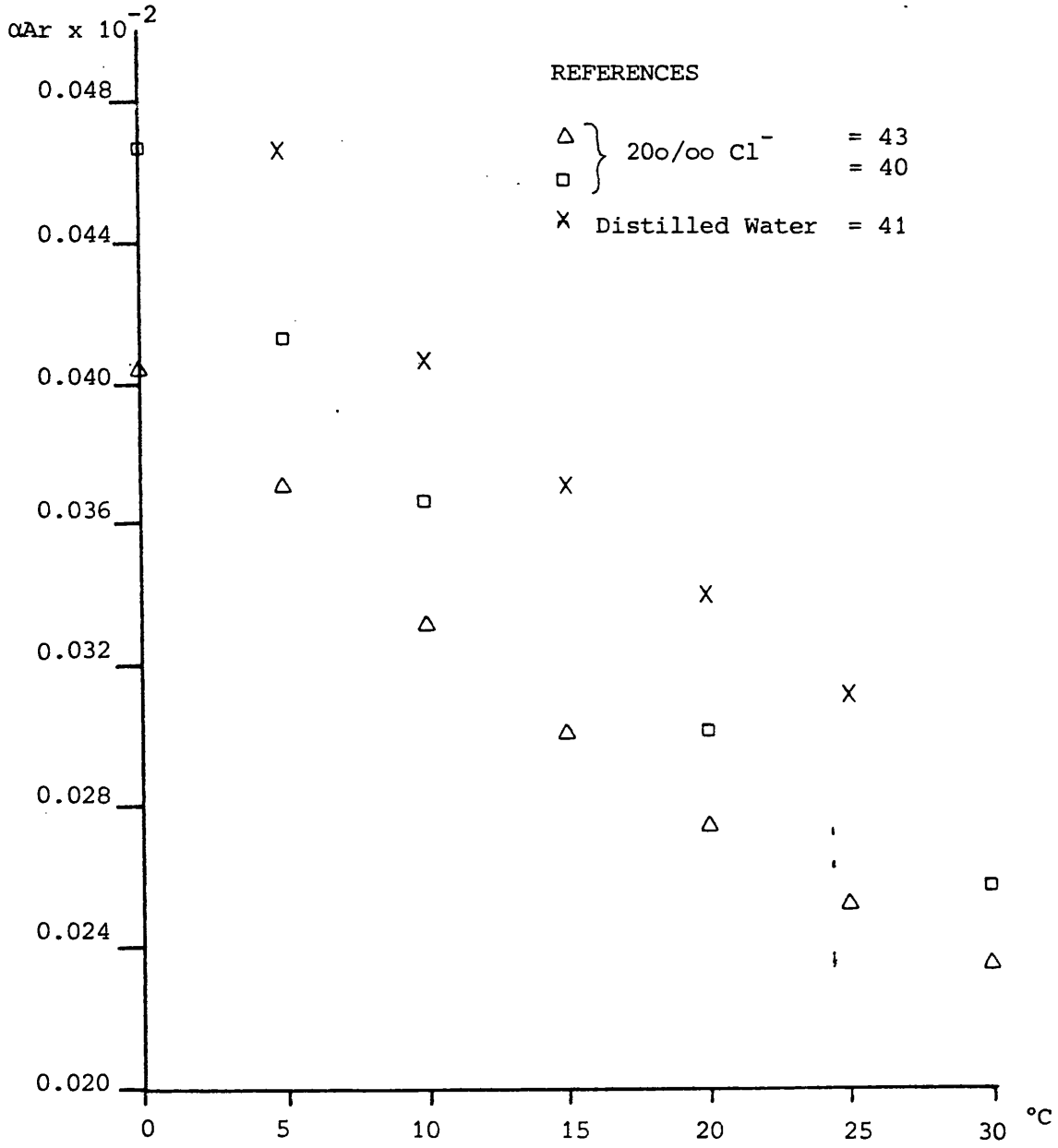
α = the solubility coefficient, the number of cm^3 of gas measured at STP, dissolved in 1l of water in equilibrium with the gas when its partial pressure in 760mm Hg.

FIGURE 1.5 A COMPARISON OF ARGON SOLUBILITY DATA



α = the solubility coefficient, the number of cm^3 of gas measured at STP, dissolved in 1l of water in equilibrium with the gas when its partial pressure is 760mm Hg.

FIGURE 1.6 THE SOLUBILITY OF NITROGEN AT 20°/00 CHLORINITY COMPARED WITH ITS SOLUBILITY IN DISTILLED WATER



α = the solubility coefficient, the number of cm^3 of gas measured at STP, dissolved in 1l of water in equilibrium with the gas when its partial pressure is 760mm Hg.

FIGURE 1.7 THE SOLUBILITY OF ARGON AT 20°/00 CHLORINITY COMPARED WITH ITS SOLUBILITY IN DISTILLED WATER

has been derived[41].

$$\ln(1/K) = A_3(\frac{T1}{T} - 1) + A_2(\frac{T1}{T} - 1)^2$$

where K is Henry's coefficient given in atmospheres by

$$K = \frac{124.4142\ \rho\ Z_o\ Z_e\ x\ 10^4}{\beta} \text{ (in atm)}$$

and Z_o = the gas compressibility factor at 0°C, 760 torr

Z_e = the gas compressibility factor under equilibrium conditions

ρ = density of water at equilibrium temperature

(for an ideal gas $Z_o = Z_e = 1$)

β = Bunsen coefficient.

T1 = absolute temperature at which Henry's coefficient K hypothetically would be unity

A_2 = 36.855 a dimensionless constant

A_3 = a dimensionless constant

This relationship explains well the solubility measurements of previous workers. Accordingly the solubility ratios of N_2 and Ar dissolved in groundwaters over a range of temperatures were calculated using this equation (Appendix A).

1.4.3 THE OXIDATION STATES OF NITROGEN

Nitrogen exhibits oxidation states from +5 to -3 (Table 1.3). For most of the aqueous range of Eh (figure 1.8), N_2 is the most stable species[44]. Each species, NH_4^+, NO_2^- and NO_3^- has a dominant zone within a narrow Eh range from +338 to +420 mv. In reducing conditions ammonia predominates whereas for Eh +932 mv, NO_3^- dominates at pH 7. The redox transformations release energy which is utilised by the mediating bacteria[45].

TABLE 1.3 OXIDATION STATES OF NITROGEN COMPOUNDS

OXIDATION STATE	EXAMPLE N SPECIES
5	N_2O_5; HNO_3; NO_3^-
4	NO_2; N_2O_4
3	HNO_2; NO_2^-
2	NO
1	N_2O; $H_2N_2O_2$; $N_2O_2^{2-}$
0	N_2
-1	NH_2OH
-2	N_2H_4; $N_2H_5^+$
-3	NH_3; NH_4^+

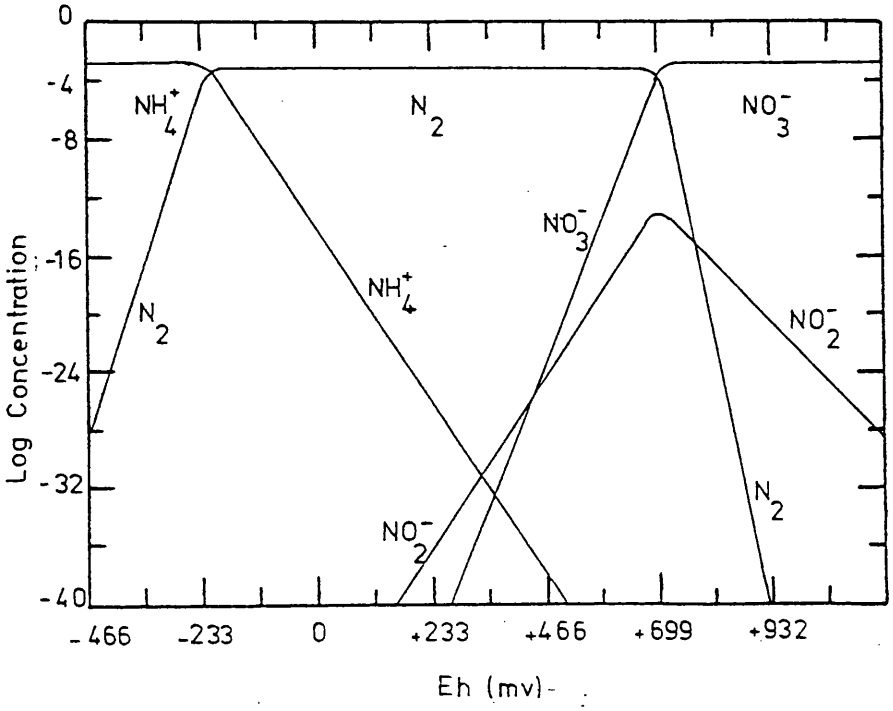


FIGURE 1.8 EQUILIBRIUM DISTRIBUTION OF NITROGEN COMPOUNDS AS A FUNCTION OF Eh AT pH 7 & 25°C. TOTAL CONCENTRATION IS 10^{-3} GRAM ATOMS OF N PER LITRE. MAXIMUM N_2 CONCENTRATION IS THEREFORE 5×10^{-4} M, CORRESPONDING TO ABOUT P_{N_2} OF 0.77 ATM[44].

In confined aquifers, the oxidizing conditions of the recharge area typically change to a reducing environment downdip[46,47]. NO_3^- is stable in the recharge area, and may be denitrified as the dissolved oxygen concentration diminishes[19]. The overall chemistry of an aquifer evolves to reduced species[48,49] and NH_4^+ is the major ion.

1.5 NITROGEN STABLE ISOTOPE GEOCHEMISTRY

The natural variations in N isotope abundance, designated as $\delta^{15}N$ are expressed as parts per thousand difference from the $^{15}N/^{14}N$ ratio in a standard, usually atmospheric N_2.

$$\delta^{15}N = \frac{(^{15}N/^{14}N)x - (^{15}N/^{14}N)\ atm}{(^{15}N/^{14}N)\ atm} \times 1000°/00$$

where x = the sample.

A positive $\delta^{15}N$ indicates enhancement of the heavier isotope with respect to air, and a negative value, a lower ^{15}N concentration. The natural variations in N isotope ratios are small and correspond to $\delta^{15}N$ in the range of ±10°/00. Fractionation of the stable isotope ratio between a known source and the product can yield information on the rates and pathways of hydrogeochemical processes.

1.5.1 NITROGEN ISOTOPE FRACTIONATION

The fractionation factor, α, describes the isotope effect between reactants and products and is given as the ratio of reaction rates between each isotope species

$$\alpha = K\ (^{15}N)/K(^{14}N)$$

where the enrichment factor, ε, is defined as $(\alpha-1) \times 1000$.

The isotope ratio of a nitrogen compound is the result of:

i) physical fractionation;

ii) chemical equilibrium fractionation;

iii) chemical kinetic fractionation;

iv) the stable isotope ratio of the source material.

Physical fractionation occurs by diffusion through a porous or aqueous media, by dissolution of molecular nitrogen in water, by evaporation of volatile nitrogen compounds and by ion exchange. The diffusion process is strictly mass dependent and the kinetic fractionation factor is defined as

$$\alpha = (M_1/M_2)^{\frac{1}{2}}$$

where M_1 and M_2 are the masses of the light and heavy molecules. The carrier diffusion effect[50] (where separation of a mixture occurs by diffusion through an added gas component) has been invoked[51] to account for fractionation of nitrogen in natural gas. Small fractionation effects have been observed[52,53] for the dissolution of molecular N_2, with the dissolved N_2 having an α of 1.00085 (±0.00010) with respect to the gaseous phase. Although small, this effect is significant when studying the denitrification of nitrogen in water. Volatilization of NH_3 from a NH_4^+ solution results in the ^{15}N enrichment of the solution, and is important in relation to fertilizer application studies[54]. Ammonium is also fractionated by ion exchange processes[55], but in the natural system the effect is not so pronounced[56].

Chemical equilibrium fractionation is the concentration of an isotope in one species of a chemical equilibrium reaction. Values for isotope equilibrium constants are dependent upon the different energy levels of the molecules[57], and are calculated from partition functions.

Chemical kinetic fractionations occur in non-equilibrium reactions which are typical of biogeochemical systems. These reactions are a function of temperature, humidity, oxygen and water content of the environment, and the organic matter and mineralogical composition. If a reaction does not go to completion, as in a natural open system then ^{14}N is generally preferentially concentrated in the product, while ^{15}N is concentrated in the reactant [58]. The relative importance of physical, chemical equilibrium and chemical kinetic fractionations in the isotopic fractionation of nitrogen transformation processes is not well understood.

The fixation of N_2 by Azobacter vinelandii showed a kinetic fractionation factor of 1.0022[59,60], with the $\delta^{15}N$ of N_2 being -2.2°/00. Spurious fractionation was noted during N_2 fixation causing $\delta^{15}N$ values of + 5 to - 8°/00[56,61]. Direct assimilation of N_2 favours the lighter isotope[62,63]. Nitrogen mineralization gives a product NH_4^+ depleted in ^{15}N with $\delta^{15}N$ values ranging from -4.6 to -10°/00[64,67]. During the oxidation from NH_4^+ to NO_3^- a further depletion in ^{15}N by several per mil has been observed[56,65,68]. Fractionation is thought to occur in only the first stage $NH_4^+ \rightarrow NO_2^-$ of the two stage process[69].

Denitrification occurs via a series of intermediate steps producing a complicated kinetic effect[58]. Pure cultures of Pseudomonas stutzeri preferentiallly denitrified $^{14}NO_3^-$ and $^{14}NO_2^-$ with a fractionation factor of 1.02[70]. The kinetic isotope effect resulting from the rupture of the N-O bond yields a theoretical fractionation factor still larger than the value measured[71]. Environmental conditions have a significant influence on the process and $\delta^{15}N$ values have been found[68,72-74] to range from -1 to 20.7°/oo.

Variations in fractionation factors determined experimentally for similar N transformation reactions result because of the difficulty in reproducing similar environmental conditions. Therefore it is not possible to characterise the isotopic composition of an N source or process. The theoretical fractionation factors of mathematically treated spectrographic data are to be preferred for general application[75]. (Table 1.4).

1.5.2 THE NITROGEN ISOTOPE CYCLE

The overall effect of the fractionation processes appears to maintain the nitrogen isotope cycle in a steady state (figure 1.9). The ultimate source and sink of all transformations is the atmosphere which maintains a constant $^{15}N/^{14}N$ ratio[11] of 1:272 ± 0.3. The ratio was found to be similar at different locations over the U.S.A. for a period of six months[66]. A systematic variation with altitude due to atmospheric processes was reported[67], but it was subsequently found to be constant up to an altitude of 51.6 km[10].

Measurement of the $^{15}N/^{14}N$ ratio in minerals and rocks shows a slight enrichment of ^{15}N relative to air (Appendix B). The isotope ratio for 12 minerals averaged +1.9°/00 and for 21 igneous rocks averaged +4.7°/00[67]. The less total nitrogen a rock contains, the more enriched it is in ^{15}N[68]. This may be the effect of degassing of the earth's crust to the atmosphere, and due to fractionation by passage through the porous media, the nitrogen remaining in the rocks is enriched in ^{15}N[70]. Fractionation of N isotopes between igneous rocks and the atmosphere may result from isotopic exchange reactions between N_2, NH_3 and NH_4^+[78]. Sal ammoniac from volcanoes shows a high enrichment[81,82]. Nitrogen in caliche shows only small variations in isotopic composition[81], and has a similar mean value to the $\delta^{15}N$ for nitrate in local rain of -2[85] indicating the source. Highly enriched nitrogen dissolved in

TABLE 1.4 EQUILIBRIUM FRACTIONATION FACTORS FOR VARIOUS NITROGEN SPECIES[75]

	ENRICHED SPECIES			
	NO_2 (gas)	N_2O (gas)	N_2 (gas)	NH_3 (gas)
NO gas	1.0447 (0) 1.0390 (25)	1.0435 (0) 1.0384 (25)	1.0148 (0) 1.0137 (25)	1.0033 (0) 1.0033 (25)
N_2O gas	1.00098 (0) 1.00063 (25)			
N_2 gas	1.0295 (0) 1.0250 (25)	1.0285 (0) 1.0243 (25)		
NH_3 gas	1.0414 (0) 1.0355 (25)	1.0318 (0) 1.0349 (25)	1.0115 (0) 1.0103 (25)	

(0) Temperature in °C

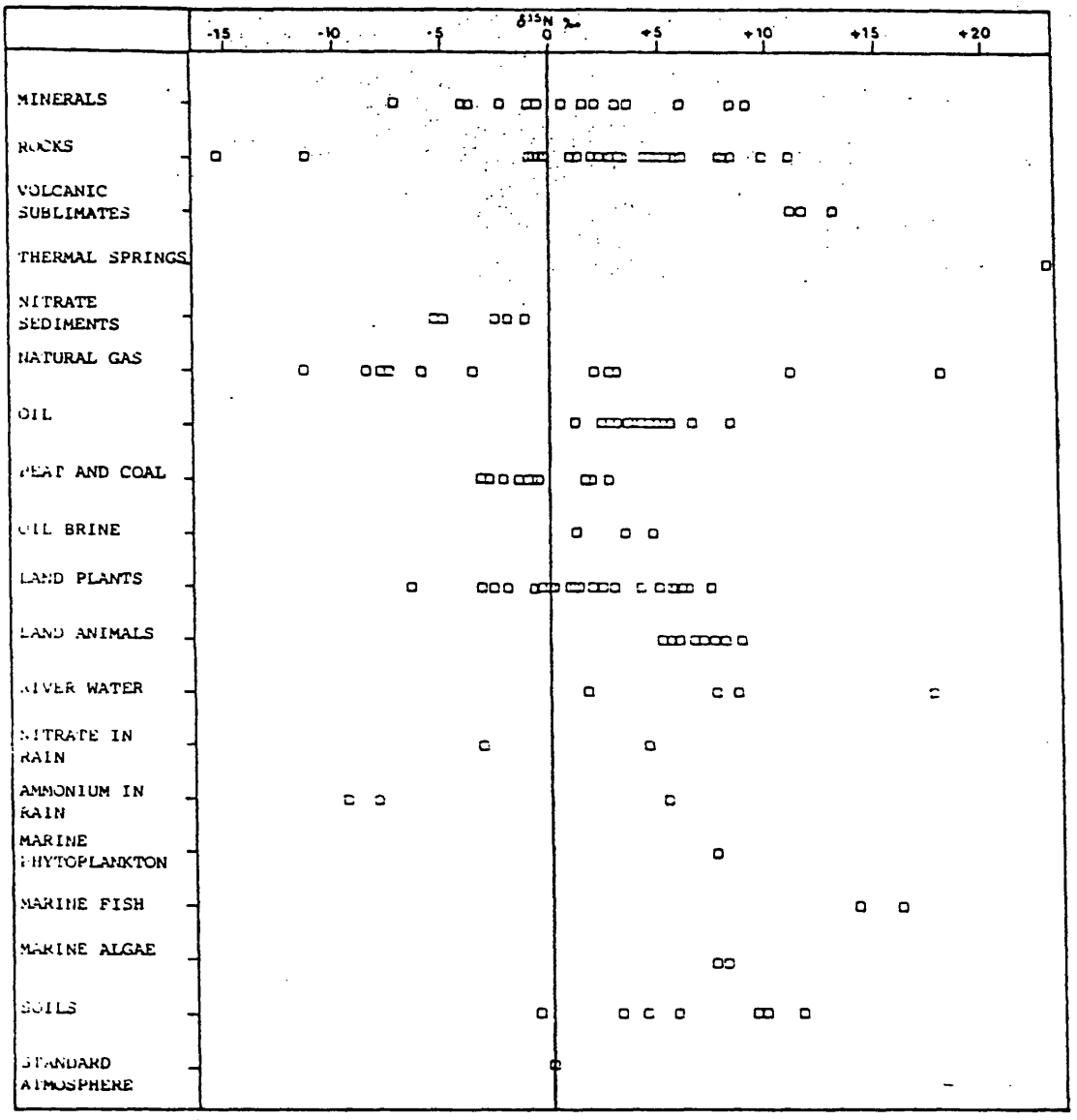


FIGURE 1.9 NITROGEN ISOTOPE FRACTIONATION IN INORGANIC AND ORGANIC MATERIALS

thermal spring water confirms a 'juvenile' origin[87].

The $^{15}N/^{14}N$ ratio of natural gases, oil and coal have been investigated[72,76,82-84] to determine their origin (Appendix B). Enrichment of ^{15}N in natural gas and mine gas indicated that the nitrogen was not derived from the associated coal because the conversion of organic nitrogen to elemental nitrogen would discriminate in favour of the lighter isotope. Natural gases associated with crude oils have a relative negative $\delta^{15}N$ value, and there is a positive correlation between low $\delta^{15}N$ values in gas and in the crude oil. A systematic trend is found in the $\delta^{15}N$ values across a gas field, demonstrating isotope fractionation from flow migration of nitrogen through the porous sandstone[84]. A similar chromatographic phenomenon in soils has been noted[56]. Crude oils show enriched $\delta^{15}N$ values with respect to those of organic nitrogen in the underlying oil brine, in which a high concentration of NH_4^+ ions are found. Therefore isotopic fractionation is caused by the extraction of hydrophilic substances into the aqueous phase leaving ^{15}N rich organic nitrogen in the oil[72].

Organic matter shows a small fractionation relative to atmospheric air (Appendix B). In plants both positive and negative $\delta^{15}N$ occur, while in animal tissue the heavier ^{15}N is favoured. These variations of $^{15}N/^{14}N$ are explained by the kinetic isotope fractionation of biochemical reactions.

In precipitation the dissolved NH_3 is photochemically oxidized to NO_3^- with a constant kinetic isotope effect of 1.004 ± 0.001[85]. This nitrogen contributes to surface and groundwaters, but the biochemical transformations of the soil dominate the $^{15}N/^{14}N$ of these waters. Ocean waters similarly reflect the biochemical fractionation processes with an

overall mean $\delta^{15}N$ value of +7°/00[86], and the near shore marine sediments have more than 25% of total nitrogen derived from a $\delta^{15}N$ enriched terrestrial source[88].

1.6. THE USE OF $^{15}N/^{14}N$ TO TRACE NITROGEN HYDROGEOCHEMISTRY

1.6.1 $^{15}N/^{14}N$ AS A TRACER

The transformation of compounds through the nitrogen cycle has been investigated using ^{15}N enriched material, ^{15}N depleted material and natural abundance ratios[89]. ^{15}N enriched material can be diluted 40,000 to 500,000 times whereas ^{15}N depleted materials have a low tolerance for dilution of approximately 2,000 fold. The high cost and limited availability of enriched and depleted materials restrict their large scale use as tracers.

Natural nitrogen containing substances can be used as tracers, but depend on the constancy of the isotopic composition. Generally only qualitative or semi-quantitative information on the broad relationship among nitrogen cycle processes can be gained. The $^{15}N/^{14}N$ ratios of all natural substances lie within a narrow range and the separation of sources in a mixed material is impossible becuase of the cumulative isotopic effects[90,91]. It has been questioned whether measurement of natural $^{15}N/^{14}N$ variations can be used to obtain accurate quantitative information on the short term effects of a current change in environmental conditions, such as the effect of a single N input on NO_3^- levels in water[89].

1.6.2. NITROGEN ISOTOPE HYDROGEOCHEMISTRY OF THE SOIL ZONE

The soil is the interface between the atmosphere and the terrestrial

hydrosphere, and as such controls the chemistry of the nitrogen input to ground water. Nitrogen in the soil occurs as organic compounds formed by bacterial decomposition of animal and plant wastes, and as inorganic species. Nitrate and ammonium are chiefly derived from precipitation, geological sources and artificial addition by fertilizers, manure and sewage.

Variations in the natural abundance of ^{15}N in the total nitrogen of soils have been reported[69,92-97]. The $^{15}N/^{14}N$ ratio may be used to study the short term[88] and the long term effects of environmental changes on the nitrogen cycle[89]. The ^{15}N abundance of the total N in the surface horizon of soils has been determined, and found to be enhanced in general with respect to atmospheric air (Table 1.5). The upper layers of the soil show slightly but significantly enriched $\delta^{15}N$ values compared with the subsoil with a $\delta^{15}N$ of +7.95 (σ=2.62)[56,89,97,99,100].

The variation is not explained by differences in the environmental conditions or soil characteristics[97]. However, forest soils tend to have lower $\delta^{15}N$ values[93] than cultivated fields[101]. Fertilizers and green manures decrease the $\delta^{15}N$ value, while animal manures have a positive influence[97]. Soils rich in organic matter also tend to have higher $^{15}N/^{14}N$ ratios for their total nitrogen content[92].

Isotope fractionation models simplify the natural system and cannot fully explain the fractionation processes[64,66,69,102]. Chemical kinetic fractionation has been demonstrated where oxidation of an ammonia based fertilizer results in a ^{15}N enriched reactant. Similarly, in denitrification the residual NO_3^- is enriched[69,63,101]. The products of these reactions gradually attain a constant $^{15}N/^{14}N$ ratio reflecting that of the total N of the soil, except where severly polluted. Soil N

TABLE 1.5 $^{15}N/^{14}N$ RATIOS OF THE TOTAL N IN THE SURFACE LAYER OF SOILS

NUMBER OF SAMPLES	MEAN $\delta^{15}N$ o/oo	RANGE	σ	REFERENCE
15	+11.7	+8.0 → 14.4	1.69	95
19	+9.7	+6.8 → 13.3	1.72	69
25	+4.32	-3.3 → +18.1	5.65	102
21	+6.09	-1 → +16	5.45	92
139	+9.22	90% +5.1 → 12.3	2.10	97
10	+3.03	+1.86 → +4.08	0.7	93
12	-0.51	-4.4 → +3	2.46	94

acts as a buffer to the incoming N and $^{15}N/^{14}N$ ratio is diluted if the additive has a positive $\delta^{15}N$, such as NO_3^- based fertilizers, or increased for additives with negative $\delta^{15}N$, such as NH_4^+ based fertilizers. Mixing of the added and natural N is time dependent, and differs under various soil types and conditions[63,91,101].

The passage of fertilizers through the soil zone has been studied using natural ^{15}N abundances[98]. Quantitative investigations have been much criticized[84,90,105], and the natural $^{15}N/^{14}N$ tracers at best give qualitative or roughly quantitative results[94]. The use of enriched fertilizer sources to trace nitrogen in the soil is advocated[90]. ^{15}N-labelled [$Ca(NO_3)_2$] in a lysimeter study[106], demonstrated the distribution of N (Table 1.6). The magnitude of gaseous loss appears to vary as a function of the water regime and organic matter content, since under more fertile soil conditions the N is immobilized rather than denitrified.

Denitrification[107,108] is moisture dependent because the percentage of soil saturation will determine the extent of anaerobic conditions. There are two types of pores in the soil, micro or capillary pores (1-6μ) and macropores (>6μ). Bacteria inhabit the internal surfaces of the micropores which are filled with water at field capacity, and maintain a constant rate of denitrification. If the water content rises to saturation point, the macropores are filled, and with increased anaerobic conditions bacteria colonize these pore surfaces and the rate of denitrification is increased[109]. The NO_3^- ion is the most soluble N species and is readily leached from the soil; a negative correlation between precipitation and denitrification has been noted[97]. Leaching losses of N_2O, comprising a small part of the total soil N, must also be considered where denitrification occurs[110,111]. The higher rates of denitrification occur where NO_3^- is concentrated[112]. Therefore,

TABLE 1.6 THE SINKS FOR SOIL NITROGEN DETERMINED BY LYSIMETER STUDIES[108]

% OF TOTAL SOIL N	SINK
<2	Runoff
30	Leached to percolate
25 - 30	Recovered by Crop
10 - 30	Remained in soil
6 - 26	Lost as N_2 by Denitrification

denitrification reflects a balance between substrate availability, oxidizable carbon content[73], the moisture regime and plant competition[69].

A dynamic equilibrium exists between nitrification of organic matter in the upper layer of a soil profile, and denitrification in the lower levels, as indicated by the mean difference in $\delta^{15}N$ values. The amount of NO_3^- in the profile is dependent upon land use. Fertilized arable and ley soil have high concentrations, fertilized permanent grassland intermediate concentrations, and unfertilized grasslands low concentrations of NO_3^- [113]. Aeration of the soil be ploughing favours nitrogen mineralization and the compact lower zones where denitrification occurs are destroyed. Increased NO_3^- levels in drainage water result, especially from ploughed grassland which releases much organic matter[103-106,114-117]. After ploughing it may take between 10 and 40 years for equilibrium to be reached again in the soil and unsaturated zone profile[107,118].

1.6.3 NITROGEN ISOTOPE HYDROGEOCHEMISTRY OF GROUNDWATER

Increased levels of NO_3^- have been reported in the main UK aquifers[4, 108-112,119-123]. Studies of mechanisms of NO_3^- movement in this zone have been made[124,125]. Evidence to suggest that significant biological action takes place at depth is limited. The bacterial population in aquifers[126], give no information on possible processes. The carbohydrate content of the Chalk has been measured and corresponds to a carbon content of $120mg/l^{-1}$ for pore water, providing enough energy to denitrify an estimated $100mg/l^{-1}NO_3N$ [127].

The nitrogen isotope hydrogeochemistry of the unsaturated zone has not been studied, so the biological contribution and the rate of denitrification can only be inferred by comparison of the isotopic evidence from the soil and saturated zones. The isotope composition of nitrate

N has been investigated to determine the source of pollution in high NO_3^- content groundwaters[5,115,117,128-131]. In all the studies the aquifers are unconsolidated Pleistocene deposits and river terraces. In a small catchment study of the relative importance of NO_3^- sources to groundwater the solid geology is overlain by limon[132-133]. The hydraulic conductivities of these aquifers are high and the soils are well drained. The hydrogeological conditions are therefore not conducive to denitrification and any high nitrate input is readily leached to the groundwater. The isotopes are subject to minimum of reactions which cause fractionation, and so source identification is possible.

In Runnels County, Texas, USA[115], two distinct nitrogen isotope ratios are distinguished in groundwater containing an average of 250mg NO_3^-/l. The predominant source is natural soil NO_3^- with a $\delta^{15}N$ of +2°/00 to +8°/00. Some wells near barnyards are polluted with animal waste and have $\delta^{15}N$ values of +10°/00 to +20°/00. Extensive terracing 20 years prior to the study caused the water table to rise and allowed the groundwater to directly leach the soil NO_3^- into the aquifer system. The positive isotope ratio of the animal waste NO_3^- is partly controlled by volatilization of $^{14}NH_3$ during decomposition of urea. The proposed process dominating the natural soil N isotope ratio is the de-animation of isotopically light protein material to $^{14}NH_3$, and not the nitrification of $NH_4^+ \rightarrow NO_3^-$. Denitrification, NH_3 volatilization and NH_4^+ adsorbtion did not appear to influence the $^{15}N/^{14}N$ ratio of the nitrate N. On Long Island, New York, USA, groundwater polluted by NO_3^- from cultivated fields can be distinguished from sewage leakage[129,134]. Ammonium type fertilizers are cited as contributing to the high NO_3^- levels of groundwater on alluvial fan aquifers in Texas, USA[130].

In the Central Platte Region, Nebraska, USA, significant negative correlations (r=-0.35), between $\delta^{15}N$ of nitrate N and the nitrate content of drainage water and between $\delta^{15}N$ and depth to the water table (r=-0.55) indicate that denitrification is occurring. Areas of low soil permeability are cited as areas of denitrification[131]. The groundwater from Runnels County, Texas has a small but positive correlation between nitrate N and its $\delta^{15}N$ (r=0.25), confirming that denitrification does not account for the $^{15}N/^{14}N$ ratio[115].

The concentration and isotopic composition of molecular nitrogen dissolved in ground water can be used to monitor the overall fluxes of nitrogen, especially resulting from denitrification. The solubility of nitrogen is primarily affected by physical parameters; temperature being dominant. The mean annual air temperature is similar to the ground temperature at the base of the unsaturated zone[135,136] and will control the solution of gases in recharging groundwater. Surface water conditions and the kinetics of near surface mechanisms may aid the enhancement of the nitrogen concentration by the addition of gas bubbles. This phenomenon has been noted in ocean waters[26,52,137], and distinguished in groundwaters[138]. During recharge small bubbles of air may become trapped in the capillary sized pores of the unsaturated zone, and be carried down below the water table[139-142]. With increased hydrostatic pressure the bubbles dissolve[142]. By comparing the concentration of N_2 with Ar the extent of the bubble solution can be measured. Argon will preferentially dissolve relative to nitrogen[144], and if only partial solution occurs, the ratio of excess N_2 to Ar would be more in proportion to the solubilities of the gases rather than their atmospheric ratio. Therefore, the nature of porosity of the unsaturated zone is significant, for small pores and narrow capillary channels will favour air entrapment.

Nitrogen derived from solution, and from excess air can be distinguished from enhanced nitrogen resulting from denitrification by graphical plotting of the excess nitrogen[138,145]. In aerobic marine environments, N_2 from the biological decomposition of organic matter has been identified using N_2/Ar ratio measurements[52,73]. In ground waters of the Auob Aquifer in the Western Kalahari the total dissolved N_2, O_2 and Ar concentrations were measured[144]. The excess nitrogen was found to increase as the NO_3^- content decreased suggesting that some N_2 was formed by reduction of the nitrate. The N_2/Ar ratio fluctuations have proved the further reduction of N_2 to NH_4^+ in groundwater before adsorbtion of NH_4^+ on clay surfaces[146].

The $^{15}N/^{14}N$ ratio of dissolved nitrogen can be used to distinguish biogenically produced gas. The nitrogen derived from solution equilibration with the atmosphere is slightly enriched with a $\delta^{15}N$ of +0.7°/00 [53]. Chemical kinetic fractionation operative in denitrification favours the lighter molecule as demonstrated by the fact that nitrogen gas from O_2 deficient Pacific Ocean water has a $\delta^{15}N$ of -30 to -40°/00 [63]. The nitrogen of biogenic origin from the Cariaco Trench in the Caribbean Sea, and Dramsfjord, Norway has been attributed to denitrification[147]. As it has a $\delta^{15}N$ ranging between +16.3 and 56.7°/00 another source must be important. The additional nitrogen produced by denitrification in groundwater has $\delta^{15}N$ ranging from -20°/00 in a sample with only a small amount of excess N_2 to -2°/00 in one with a large amount[145]. Therefore, the denitrification process favours the ^{14}N isotope, with the resulting N_2 having a $\delta^{15}N$ of approximately -20°/00. The excess air proportionately enhances the ^{15}N content, but if denitrification goes to completion then fractionation is less significant.

The permeability of the soils and geology in the recharge area are the most important factors governing the denitrification processes. If as described for various sites in the USA[5], the recharge area is highly permeable, then no denitrification occurs and nitrates from different sources, directly leached to the aquifer, may be distinguished by the $^{15}N/^{14}N$ ratio. Where the recharge area is covered by less permeable soils and the hydraulic conductivity of the aquifer is low then denitrification is probable, and can be detected by an increase in the dissolved nitrogen gas content of the water. In this situation, the $^{15}N/^{14}N$ ratio of the nitrogen cannot be used to identify a source of nitrogen input since fractionation will occur as a result of biological transformations in the soil, of movement through the porous media of both the soil and rocks, and of chemical exchange processes between fissure and pore water[19].

In the confined zone of an aquifer, these fractionation processes will still operate, but since it is a closed system the $^{15}N/^{14}N$ ratio of the dissolved N_2 is a product of the total nitrogen flux and may be used to determine the relative importance of the processes. In the Auob sandstone aquifer[145] of the Western Kalahari the denitrification of low concentrations of nitrate ($0.11 mgl^{-1}$ to $0.25 mgl^{-1}$) was estimated to take 14000 years, where the groundwater flow rate was 2m/year. The fractionation factor of the reaction was calculated as $\varepsilon = -30 \pm 6°/00$ and agrees with other biologically mediated denitrification measurements. However, denitrification in this example is very slow, and physical fractionation must not be neglected. No interpretation of fractionation processes in the unconfined zone can be made, since the system is open and nitrogen gas may escape.

In the preceding review of the known groundwater nitrogen cycle, it has been shown that the relative importance of the chemical, physical and biological transformations are not clear. In this study two carbonate aquifers with differing hydrogeological conditions were investigated and the conclusions from these case studies have been incorporated into a model of nitrogen hydrogeochemistry. The importance of the recharge conditions are stressed in the interpretation of nitrogen tracer work to define the aquifer processes. With this better understanding a more accurate prediction is made of the capacity of these aquifers to maintain low nitrate water supplies.

2. FIELD, CHEMICAL AND MICROBIOLOGICAL TECHNIQUES

2.1 FIELD MEASUREMENTS

To establish the geochemical control of nitrogen species in groundwaters the physico-chemical environment and microbiological ecology were investigated.

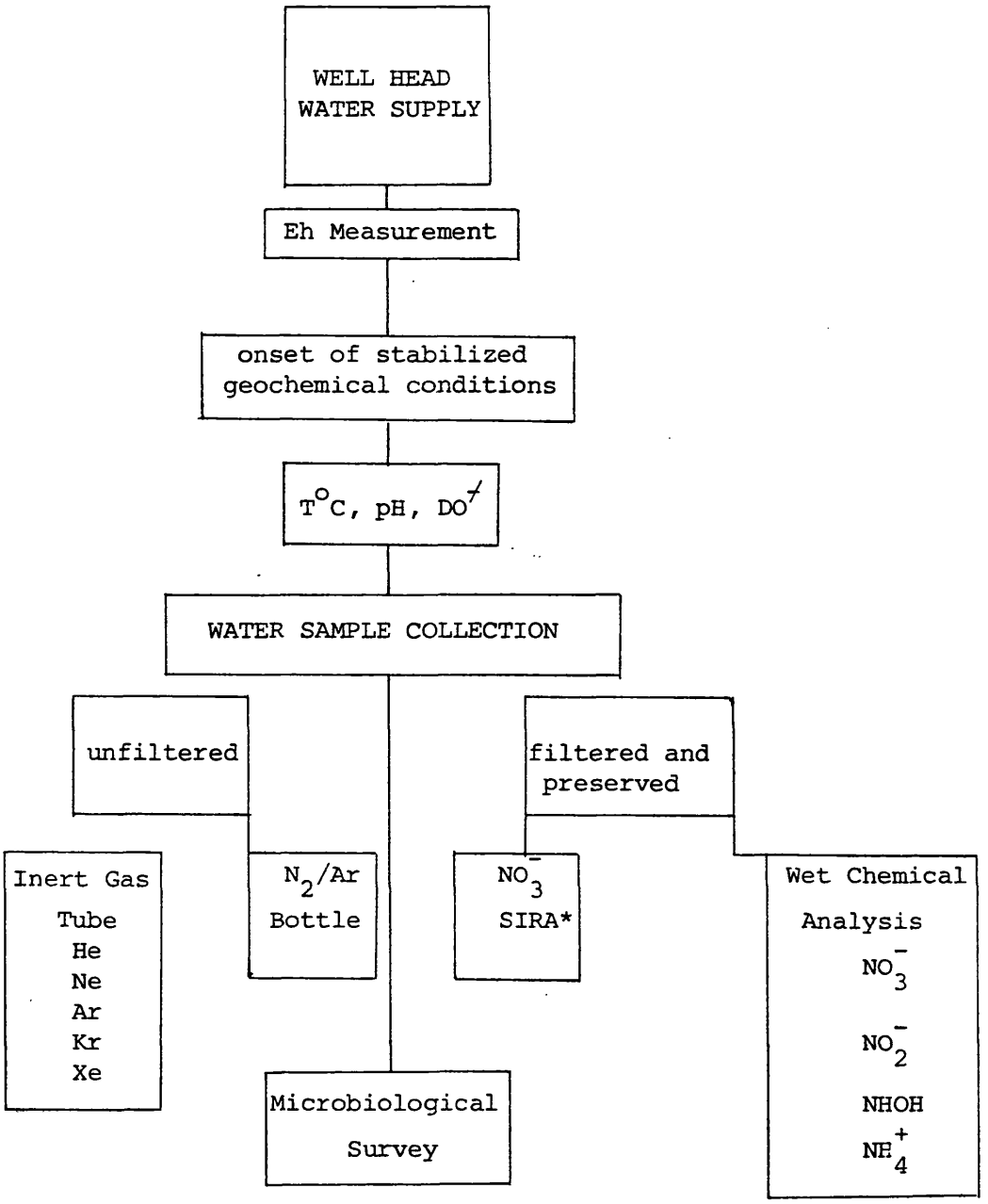
At each sampling site measurements of temperature, pH, redox potential (Eh), dissolved oxygen content and nitrite concentrations were taken. Used in conjunction with data collected for other chemical species, the evolution down dip of the hydrogeochemistry of an aquifer was traced. A sequence of field tests was followed (figure 2.1).

To ensure that the water sampled was representative of the aquifer, the redox potential was monitored at the well head. Once a constant value was obtained, the other field measurements were taken. The collection of samples for the various laboratory analyses was then carried out.

2.1.1 TEMPERATURE

Temperature was determined since it was necessary to the calculation of the concentration of dissolved gases, and to correct for the solubilities of inorganic solutes.

Measurement of the temperature was made to the nearest 0.5°C, with a mercury filled glass thermometer. When sampling a borehole with a standing water level, a dissolved oxygen/temperature probe (EIL Model 1520) was lowered down the hole. The scale ranged from -5°C to +35°C with a stated accuracy of ±1°C.



/ DO = Dissolved Oxygen

* SIRA = Stable Isotope Ratio Analysis

FIGURE 2.1 A FLOW CHART OF FIELD MEASURING AND SAMPLING TECHNIQUES

2.1.2 pH

pH in part controls the stability of dissolved nitrogen species in water, especially the solubility of ammonia, for NH_3 is present at high pH's while ionic ammonia, NH_4^+ is present at low pH's[21]. Therefore, pH was determined in[148] the field with an Extech Digital 607 pH meter, calibrated with buffers of pH4 and pH7. The mean of three consecutive readings that differed by no more than ±0.05 of a pH unit was recorded.

2.1.3 REDOX POTENTIAL (Eh)

Eh is a measure of the potential of a platinum electrode in a solution against a calomel electrode. In groundwater chemistry the oxidation-reduction reactions are generally not reversible and so a quantitative treatment applying the Nernst equation is not suitable. In this study, Eh is used as a qualitative measure[46] of the oxidation reduction potential, indicating reduced chemical conditions and the predominant dissolved nitrogen species.

Eh was monitored with an Orion combination platinum electrode 96-78-00, filled with Orion solution 90-00-01. The accuracy and reproductivity were checked using two reference solutions (Table 2.1) of differing potassium ferri-ferro cyanide concentrations[149,150].

Since the redox potential was controlled by the dissolved oxygen content of the water, the electrode was enclosed in a flow cell[149,151], to exclude atmospheric air (figure 2.2). A controlled water supply ensured no interference from streaming potentials.

TABLE 2.1 Eh REFERENCE SOLUTIONS[150]

	REAGENTS		ELECTRICAL POTENTIAL mV
SOLUTION A	0.1M	$K_4Fe(CN)_6.3H_2O$	192
	0.05M	$K_3Fe(CN)_6$	
SOLUTION B	0.01M	$K_4Fe(CN)_6.3H_2O$	258
	0.05M	$K_3Fe(CN)_6$	
	0.04M	$KF.2H_2O$	

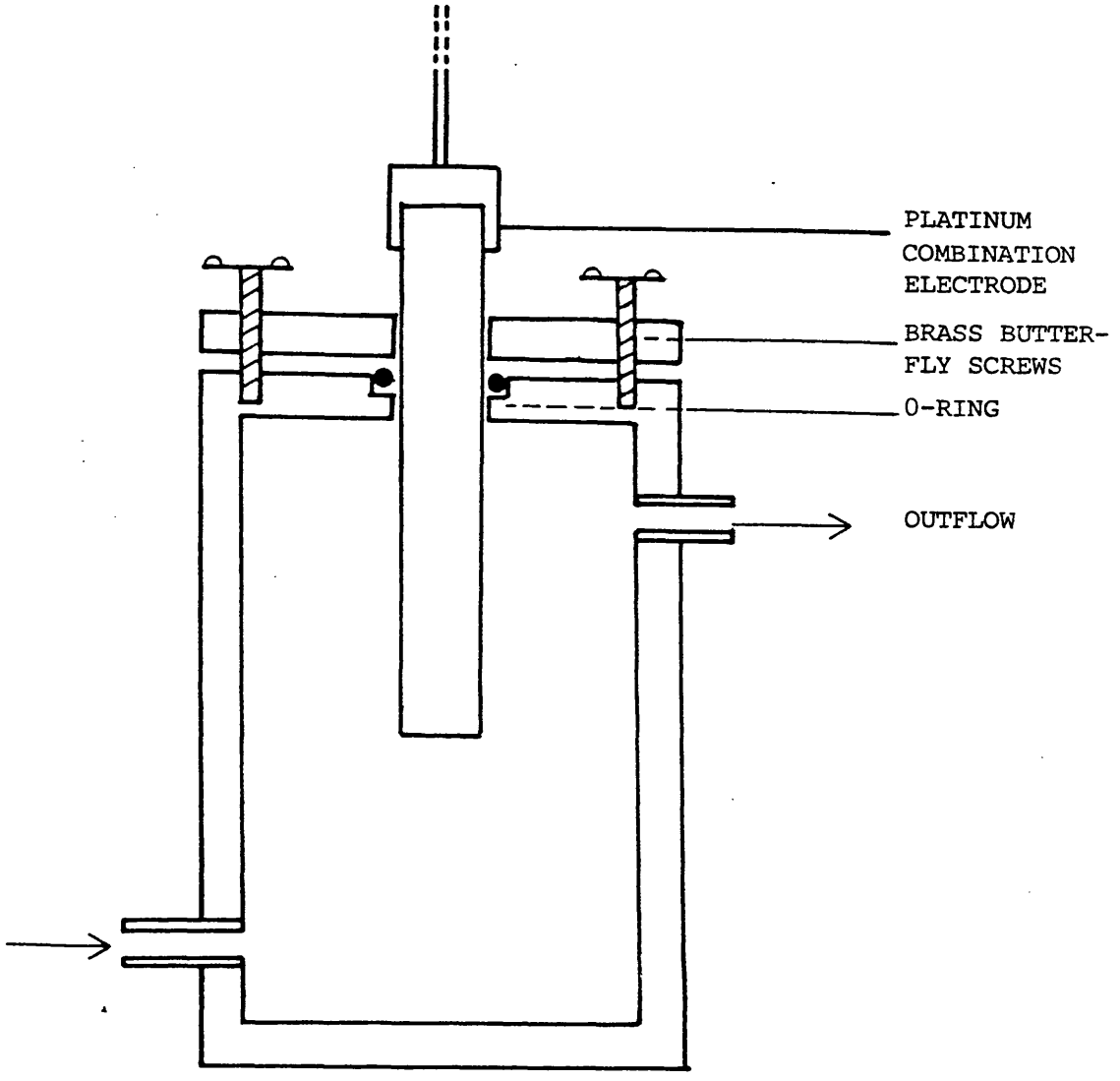


FIGURE 2.2 THE FLOW CELL CONTAINING THE Eh ELECTRODE

2.1.4 DISSOLVED OXYGEN

Oxygen concentration in groundwater was measured to identify anaerobic conditions, for not until oxygen had been reduced to zero would the process of denitrification commence.

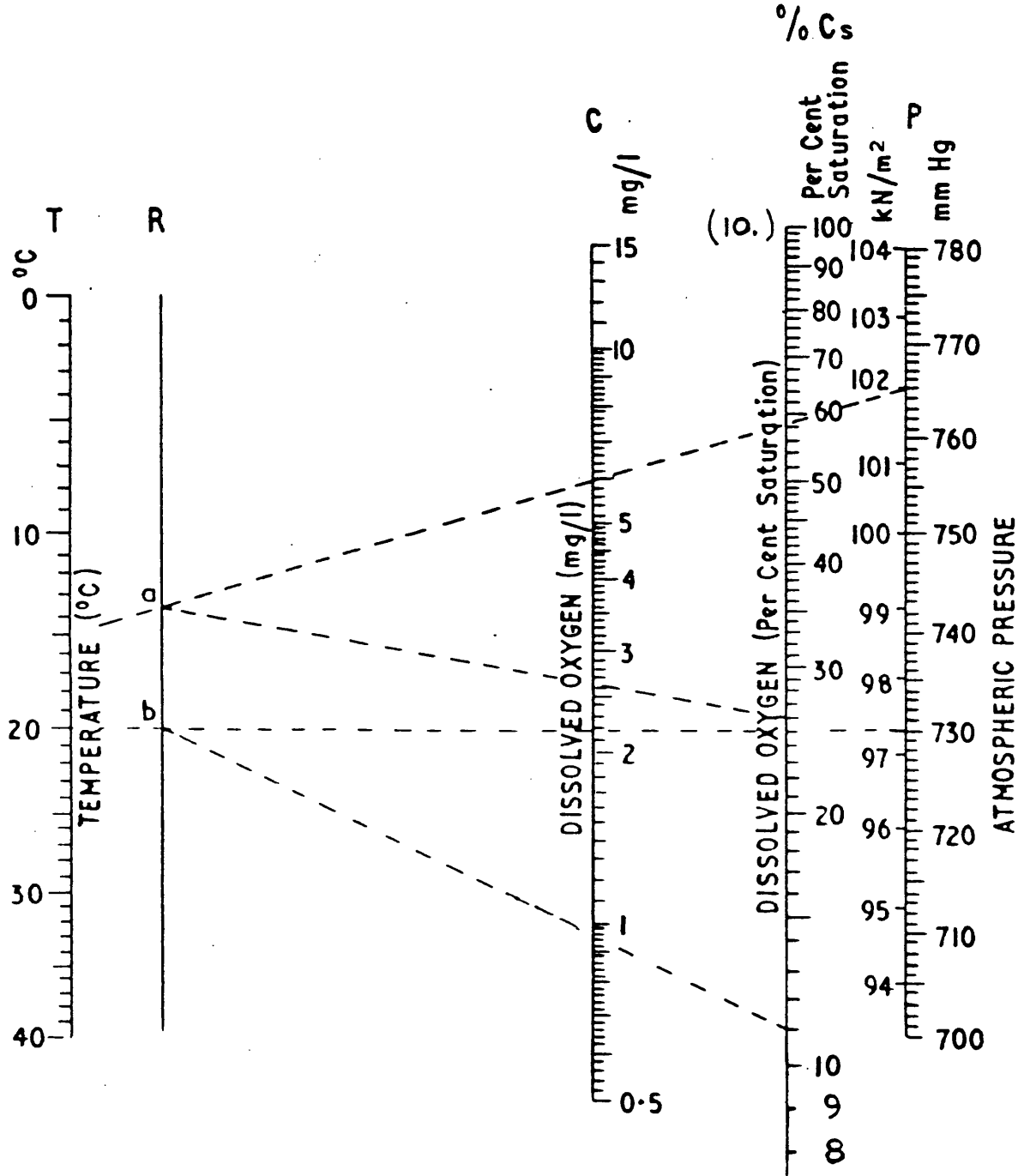
Wet chemical methods are commonly used for laboratory determination of dissolved oxygen[152], but were not suitable for this field study. A dissolved oxygen meter (Electronic Instruments Ltd, Model 1520) and electrode (Model A15A) were used. They were calibrated in the laboratory before use, and a saturated sodium sulphite solution was used as a deoxygenated reference in the field.

Measurement was made on a nonaerated water sample at the well head. The percentage oxygen saturation readings were converted to mg/l^{-1} using a graphical procedure (figure 2.3), taking account of the temperature and atmospheric pressure. The system had a stated[153] accuracy of ±1%.

2.1.5 NITRATE

The approximate NO_3^- content of the groundwater was determined in the field, so that the necessary volume of water could be collected for subsequent isotopic analysis of NO_3.N.

A Corning Liquid Ion Exchange Nitrate Electrode (Catalogue No: 476134) was used, and calibrated in the laboratory using standard NO_3^- solutions. Erratic results were obtained when high HCO_3^- ion concentrations were present in the water sample.



Connect T & P to give Intersection on R. Connect point of intersection & % Cs. Read C.

Dissolved Oxygen - Determination Of Concentration (mg/l) From % Saturation.[157]

FIGURE 2.3

2.1.6 NITRITE

Nitrite is a highly unstable product of NO_3^- reduction and occurs in anoxic conditions. A field test for the presence of NO_2^- was performed to indicate areas of denitrification. Once identified these areas were then sampled to determine the dissolved N_2 gas concentrations.

An aquarium testing kit 'Tetra-Test NO_2' (Tetra Werte Dr. ter. nat Ulrich Baensch GmbH 0-4520 Melle 1, West Germany) was used. It was capable of detecting $0.2mgl^{-1}$ NO_2^-.

2.1.7 WATER SAMPLING AND PRESERVATION

Water samples were collected for the analyses (Table 2.2). Sample treatment and storage procedures were designed to prevent changes in the oxidation state of nitrogen compounds especially due to the influence of micro-organisms[184,155].

Dark brown, screw top, plastic bottles were used to eliminate light. Filtration was performed on samples using Nucleopore, 0.2µm polycarbonate membrane filters to exclude bacteria. These filters were composed of a most inert material and to avoid contamination were washed before use. Chloroform was added as a bacteriocide in the proportion of $5cm^3$ per litre of sample[156,157]. The bottles were then stored in a cool place before analysis.

Samples taken for nitrogen and inert gas analysis were untreated. Water from the well head was permitted to flow through the glass tube (figure 3.3) and the taps were sealed, ensuring that there were no entrapped gas bubbles[158]. Various types of collection bottles were designed for the different N_2/Ar ratio analysis methods, and these will

TABLE 2.2 WATER SAMPLES AND METHODS OF PRESERVATION

ANALYSIS	CONTAINER	SAMPLE VOLUME (cm^3)	FILTERED*	$CHCl_3$ ADDITION**
NO_3^-	Brown Plastic Bottle	250	✓	✓
NO_2^-	" " "	250	✓	✓
NHOH	" " "	1000	✓	✓
NH_4^+	" " "	250	✓	✓
$^{15}N/^{14}N$ ratio on NO_3^-N	Plastic Bottle	up to 25000	–	✓
$^{15}N/^{14}N$ ratio on N_2	$250cm^3$ evacuated Glass Bottle	c 125	–	–
Inert Gases	$1cm^3$ Glass Tube	1 - 2	–	–
N_2/Ar ratio	$250cm^3$ evacuated Glass Bottle	c 125	–	–

* = 0.2μ x 47mm Nucleopore Polycarbonate membrane filter

** = $5cm^3$ $CHCl_3$ to $1000cm^3$ of sample

be described with the individual techniques.

2.2 ANALYSIS OF NITROGEN SPECIES

Four ionic species of nitrogen were monitored from outcrop through the confined zone of aquifers. The ions NO_3^-, NO_2^-, $NHOH^-$ and NH_4^+ highlighted the systematic transformation from oxidized to reduced conditions.

2.2.1 A REVIEW OF NITRATE ANALYTICAL METHODS

The determination of NO_3^- has been reviewed[159]. Colorimetric methods are the most sensitive and little or no sample pretreatment is required. These methods may be grouped into categories according to the reaction utilized-nitration, oxidation, reduction and u.v. light absorbtion (Table 2.3).

The method of reducing NO_3^- to NO_2^-, followed by the 'Greiss-Ilosvay' diazotization and coupling reaction is very sensitive and specific and was used in this study. Cadmium may be used as filings or in the spongy form[171-172]. Treatment of the metal surface with $CuSO_4$[168,169] may increase the reduction power by raising the standard potential of Cd^{2+} from 0.403v to 0.740v, but this also risks reduction beyond NO_2^-. By washing cadmium with mercuric chloride an amalgam layer forms, so slightly decreasing the reduction power. Careful control of the reduction column length, structure and pH enables quantitative conversion and recovery of NO_3^-. Yields of 99% ±1% for the transformation and recovery of NO_3^- to NO_2^- have been obtained[167].

TABLE 2.3 COLORIMETRIC METHODS FOR NITRATE DETERMINATION

METHOD	ACTIVE REAGENT	COMMENT
NITRATION	Phenoldisulphonic acid[160] 2,4 xylenol[161] 2,6 xylenol[162,163] Chromotrophic acid[152]	Lengthy procedures Interference from Cl^-
OXIDATION	Brucine[164]	Interference from Cl^- > 5mg/l^{-1} and from Fe^{2+}, Fe^{3+} and Mn^{4+}
REDUCTION	HOMOGENEOUS Hydrazine and Cu II[165]	Slow reduction 24hrs needed from completion Interference from H_2S
	HETEROGENEOUS Zinc[165]	Reproduction poor
	Cadmium[167-69]	Best technique available but careful preparation
U V LIGHT ADSORPTION	A rapid analysis using ultra-violet light adsorption[170]	Interference from organic matter and Fe^{2+} > 100µgl^{-1}

In acidic media the reaction

$$NO_3^- + 2H^+ + 2e^- \gtrless NO_2^- + H_2O \quad (Eo = 0.94v)$$

occurs, whereas in neutral or alkaline media

$$NO_3^- + H_2O + 2e^- \gtrless NO_2^- + 2OH^- \quad (Eo = 0.015v).$$

The electrons are provided by the oxidation of cadmium

$$Cd = Cd^{2+} + 2e^- \quad (Eo = -0.40v)$$

2.2.2 NITRATE ANALYSIS - EXPERIMENTAL

The analysis of NO_3^- by reduction with cadmium was used in this study. Only Cl^- interferes with the reaction, by retarding the rate of reduction, but the yield of NO_2^- is unaffected[167].

2.2.2.1 Apparatus

A glass ion exchange column (figure 2.4) was packed with Cd filings, secured between glass wool plugs. The filings were made with a new rasp from a high purity Cd source. The filings were washed with acetone, 2M HCl, water and methanol, and dried 'in vacuo' before being stored over silica gel in a dessicator. They were amalgamated by shaking in a 2% solution of mercuric chloride in 0.1M HCl. The reduction column was packed by washing the filings in with pH6.9 buffer solution. Continuous tapping facilitated the packing and avoided the entrapment of air bubbles.

2.2.2.2 Reagents

pH 6.9 buffer solution, 1.00M Imidazole solution and 0.50M HCl were diluted in the proportions 1:100.

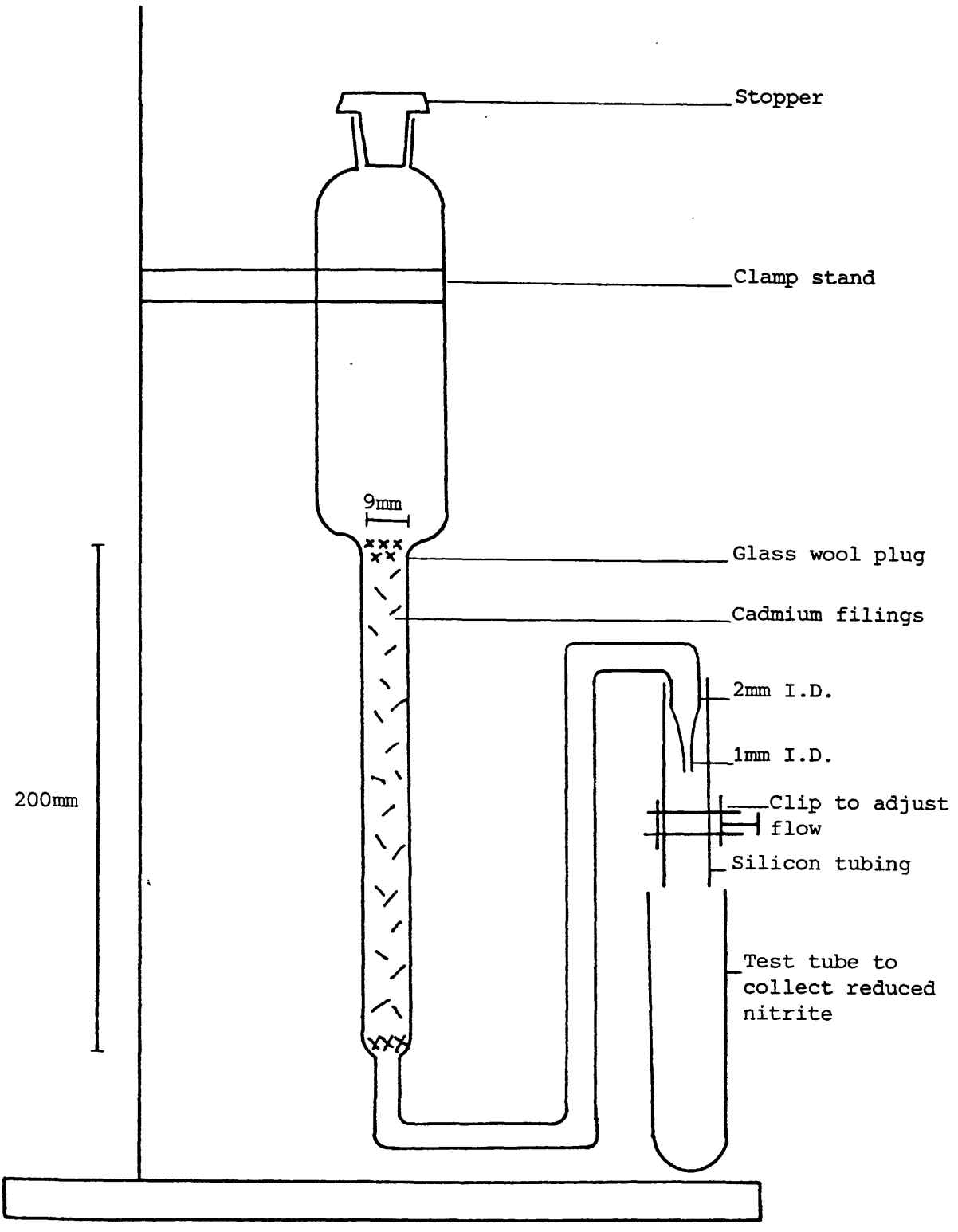


FIGURE 2.4 A NITRATE REDUCTION COLUMN

2.2.2.3 Procedure

To start the sample run 25cm^3 of 0.05M H_2SO_4 was passed through the reduction column, followed by pH 6.9 buffer solution until the effluent was neutral. The flow was adjusted until the optimum rate for reduction was obtained. 10cm^3 of sample or standard were poured on top of the column. The NO_2^- produced was collected in a test tube and stoppered immediately. Without delay the collected solution was treated with reagents for the determination of nitrite (see 2.2.4). More pH 6.9 buffer solution was added to the Cd^{2+} column so that it would not drain. Then a further 50cm^3 was flushed through before the next sample was reduced.

2.2.2.4 Calibration Results

The efficiency of reduction of a column was tested by comparing standard solutions colorimetrically. Standard $NaNO_2$ solutions were passed through the column and compared with similar untreated solutions to detect reduction beyond NO_2^-. Standard solutions of $NaNO_3$ were then passed through the column and the efficiency of reduction was determined to be 95%, with a limit of detection of 0.43mgl^{-1} NO_3^- reduced to NO_2 (Table 2.4 and figure 2.5).

2.2.3 NITRITE ANALYSIS

Methods for the analysis of nitrite have been reviewed[159]. The Greiss-Ilosvay technique was selected for this study[167]. It was first established by Greiss[173] and modified by Ilosvay[174] and is based upon the reaction of nitrite with a primary aromatic amine (diazotising agent) in an acidic solution to produce diazonium salts. The salts couple

TABLE 2.4 CALIBRATION RESULTS FOR A NITRATE REDUCTION COLUMN

CONCENTRATION OF THE STANDARD SOLUTIONS mgl^{-1}	CONCENTRATION OF STANDARD SOLUTIONS MEASURED AS ABSORBANCE UNITS		
	UNTREATED $NaNO_2$	$NaNO_2$ PASSED THROUGH COLUMN	$NaNO_3$ REDUCED
1.70	0.96	0.90	0.94
1.28	0.74	0.72	0.73
0.85	0.49	0.40	0.48
0.43	0.25	0.25	0.26
0.17	-	-	0.17
0.09	0.07	0.13	0.07

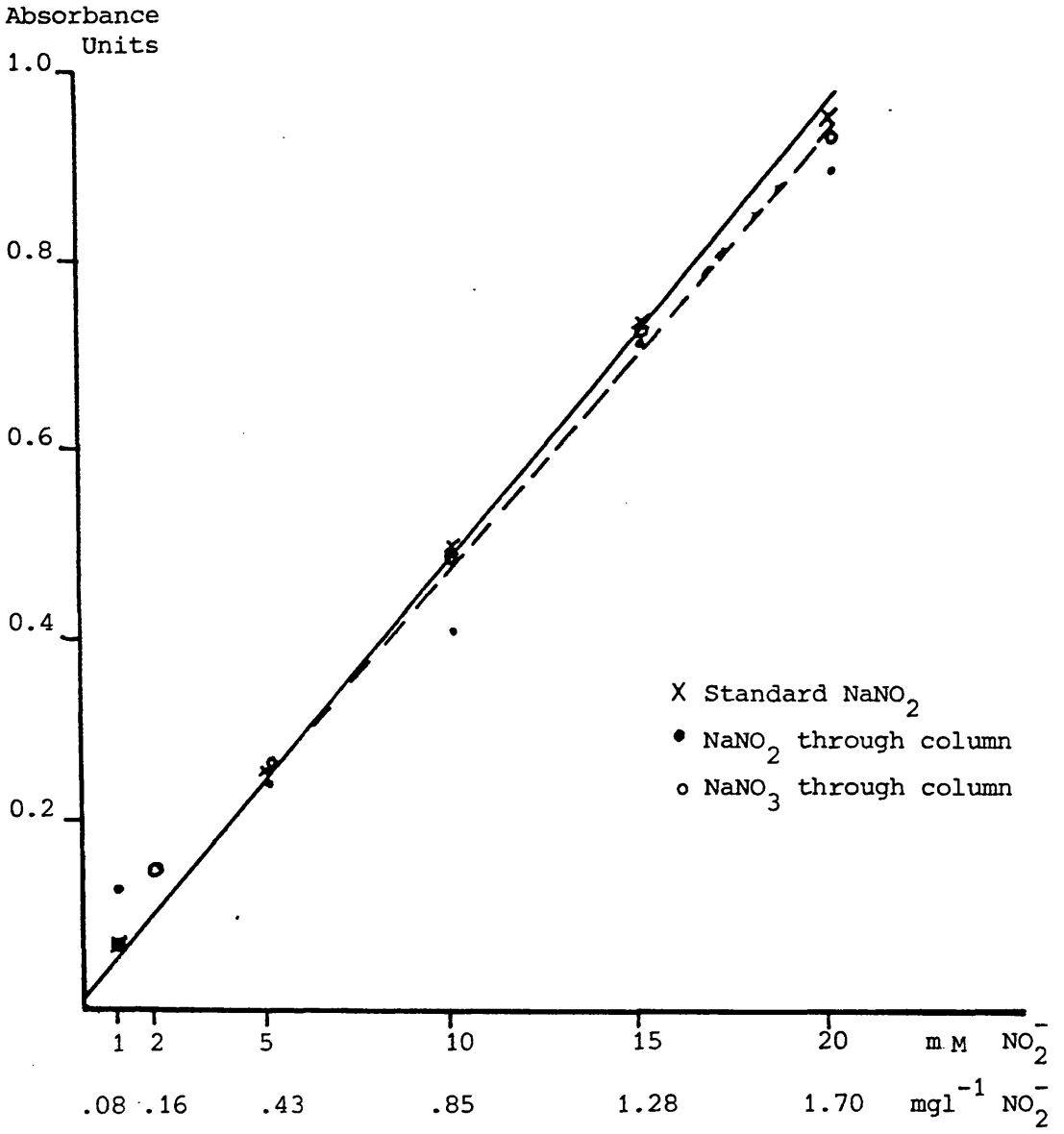


FIGURE 2.5 CALIBRATION CURVE OF NITRATE REDUCTION ON A CADMIUM COLUMN

with aromatic compounds containing amino or hydroxyl groups (coupling reagents), to form reddish-purple azo compounds which can be measured photometrically (figure 2.6).

2.2.4 NITRITE ANALYSIS - EXPERIMENTAL

2.2.4.1 Reagents

Diazotizing Reagent. 2.50g Sulphanilamide were dissolved in $50cm^3$ of HCl (1+1) and diluted to $250cm^3$.

Coupling Reagent. 2.50g N(1-naphthyl) ethylenediamine dihydrochloride were dissolved in water and diluted to $250cm^3$. The solution was kept in the dark in a refrigerator, and small quantities were withdrawn and brought to room temperature before use.

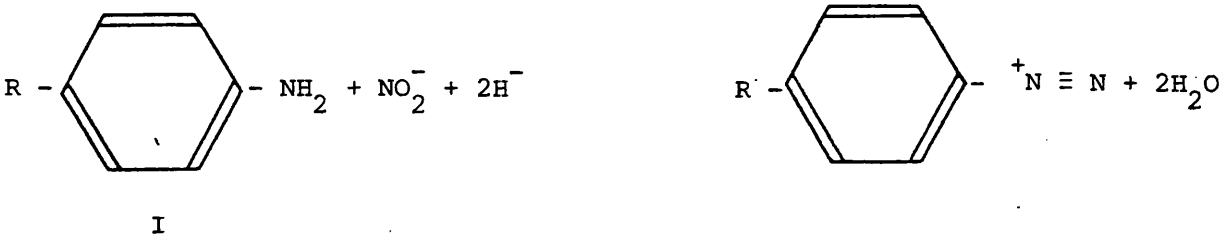
2.2.4.2 Procedure

$10cm^3$ of sample or standard NO_2^- solution were pipetted into a $25cm^3$ volumetric flask. Then with an 'Oxford sampler', 200µl of diazotizing reagent were added and mixed by swirling. After 5 minutes, 200µl of coupling reagent were added. After a further 15 minutes, the absorbance at 543nm was measured in a spectrophotometer (Unicam SP500, Series 2). Measuring cells with a 1cm path length were used for normal work, and for very dilute solutions 4cm cells were used.

2.2.4.3 Calibration Results

The results are given in the form of a calibration curve (figure 2.7). The lowest limit of detection was found to be 0.05mg NO_2^-/1.

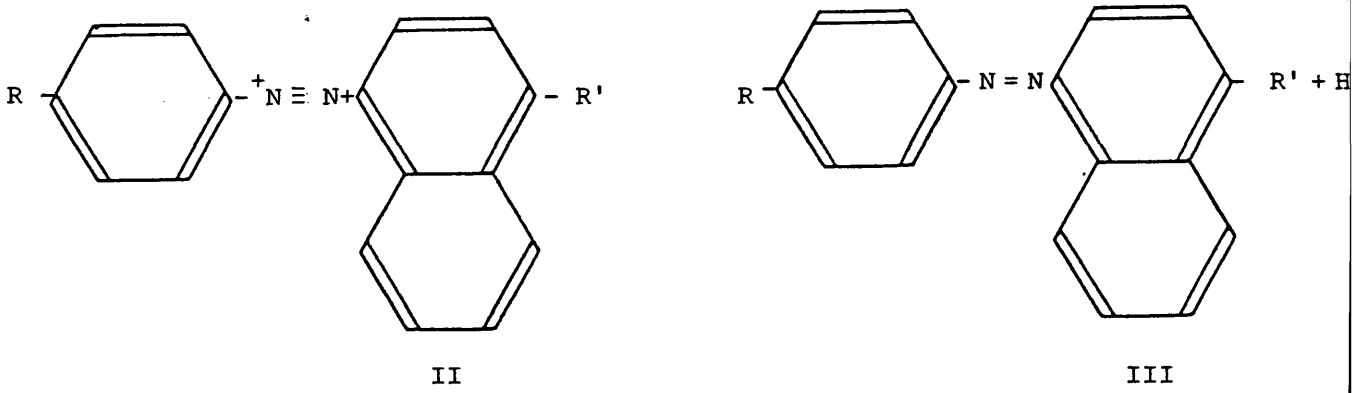
DIAZOTIZATION REACTION:



I

I = Sulphanilamide

COUPLING REACTION:



II

III

II = N (1-naphthyl) ethylenediamine (R' = $NH.CH_2.CH_2.NH_2$)

III = Azo compound

FIGURE 2.6 THE GREISS-ILOSVAY REACTION

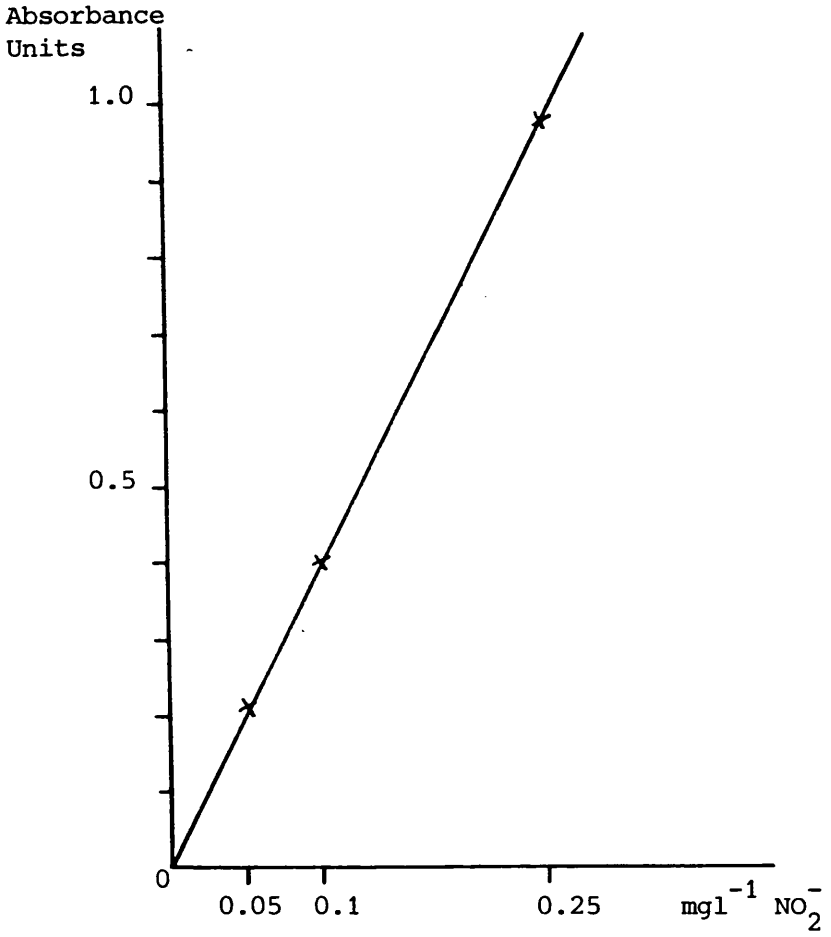


FIGURE 2.7 THE NITRITE CALIBRATION CURVE

2.2.5 A REVIEW OF ANALYTICAL METHODS FOR AMMONIUM

The selection of a method for ammonia analysis was dependent upon the concentration of the cation and upon the presence of interfering substances, such as alkaline earth metals. Direct determination of low concentrations of NH_4^+ is possible. Greater precision is achieved with preconcentration by distillation, but this is subject to the formation of NH_4^+ from other nitrogen compounds[152].

After study of the various methods (Table 2.5), the oxidation procedure was found to be most suitable. A very sensitive method uses the hypochlorite ion to oxidize NH_4^+ to NO_2^- in the presence of bromide ions.

$$NH_4^+ + 2HOCl + 2Br_2 \rightarrow NO_2^- + 4HBr + 2HCl$$

The nitrite concentration is then determined by the Greiss-Ilosvay procedure. Modifications have been proposed[168] to eliminate erratic results, for a major source of error was found to be the variable decomposition of NO_2^- following an acidification stage[175]. The oxidation time was successively reduced from 3.5 hours[168] to 17 minutes[175], to 1 minute[176] in the chosen method. Shortening the oxidation period eliminates interference from organic nitrogen containing compounds.

2.2.6 AMMONIUM ANALYSIS - EXPERIMENTAL

2.2.6.1 Reagents

Ammonium free deionized water.

7% KBr solution. 35g KBr were dissolved in 500cm^3 of 2.5M NaoH.

TABLE 2.5 METHOD FOR THE ANALYSIS OF LOW CONCENTRATIONS OF AMMONIUM IN GROUNDWATER

METHOD	REAGENT	COMMENT
Photometric	i) Indophenol blue[177-178]	Low sensitivity good reproducibility; organic N compounds do not interfere
	ii) Nesslerization[152]	
	iii) Rubazoic acid[168]	Time consuming pyridine needed
	iv) Hypobromite oxidation[179-180]	Hypobromite easily reduced by organic compounds
	v) Oxidation to Nitrite[175,176,181]	Very sensitive
Titrimetric	i) Sulphuric acid titration[152]	Needs prior distillation
Electrometric	i) Ion specific electrode	Poor sensitivity and interference from major cations

0.2M NaOCl solution. The concentration was determined by iodimetry. The solution was stored in an amber bottle, and it remained stable for a week at room temperature.

Arsenite solution. 1g of As_4O_6 and 0.5g NaoH were dissolved in $50cm^3$ of water and diluted to $500cm^3$.

Sulphanilamide solution. 1g of sulphanilamide was dissolved in $100cm^3$ of 3.5M HCl.

N-1 (naphthyl) ethylenediamine solution. 0.1g N-1 (naphthyl) ethylenediamine dihydrochloride was dissolved in $100cm^3$ of water and stored in an amber bottle in a refrigerator.

Oxidizing solution. $5cm^3$ of 0.2M NaOCl was added to $50cm^3$ 7% KBr solution. The solution was stored in an amber bottle and was stable for approximately one hour at room temperature.

2.2.6.2 Procedure

$25cm^3$ of sample were placed in a stoppered $50cm^3$ volumetric flask and kept at 35°C in a water bath. $2cm^3$ of oxidizing solution were added and mixed well. After 2 minutes, $1cm^3$ of arsenite solution was added to poison the oxidation reaction. Then $2cm^3$ of sulphanilamide and $1cm^3$ of N(1-naphthyl) ethylene solution were immediately added and mixed. after 5 minutes the absorbance at 543nm was measured in a 4cm cell in a spectrophotometer (Unicam 500, Series 2). By the same procedure a blank absorbance was measured, using 25ml of the ammonia free deionized water. This method was so sensitive that the analysis had to be performed in a room which was free from NH_3 and N_2O gases.

2.2.6.3 Calibration Results

A calibration curve (figure 2.8) was produced. The detection limit was 0.06mg NH_3N.

2.2.7 HYDROXYLAMINE ANALYSIS

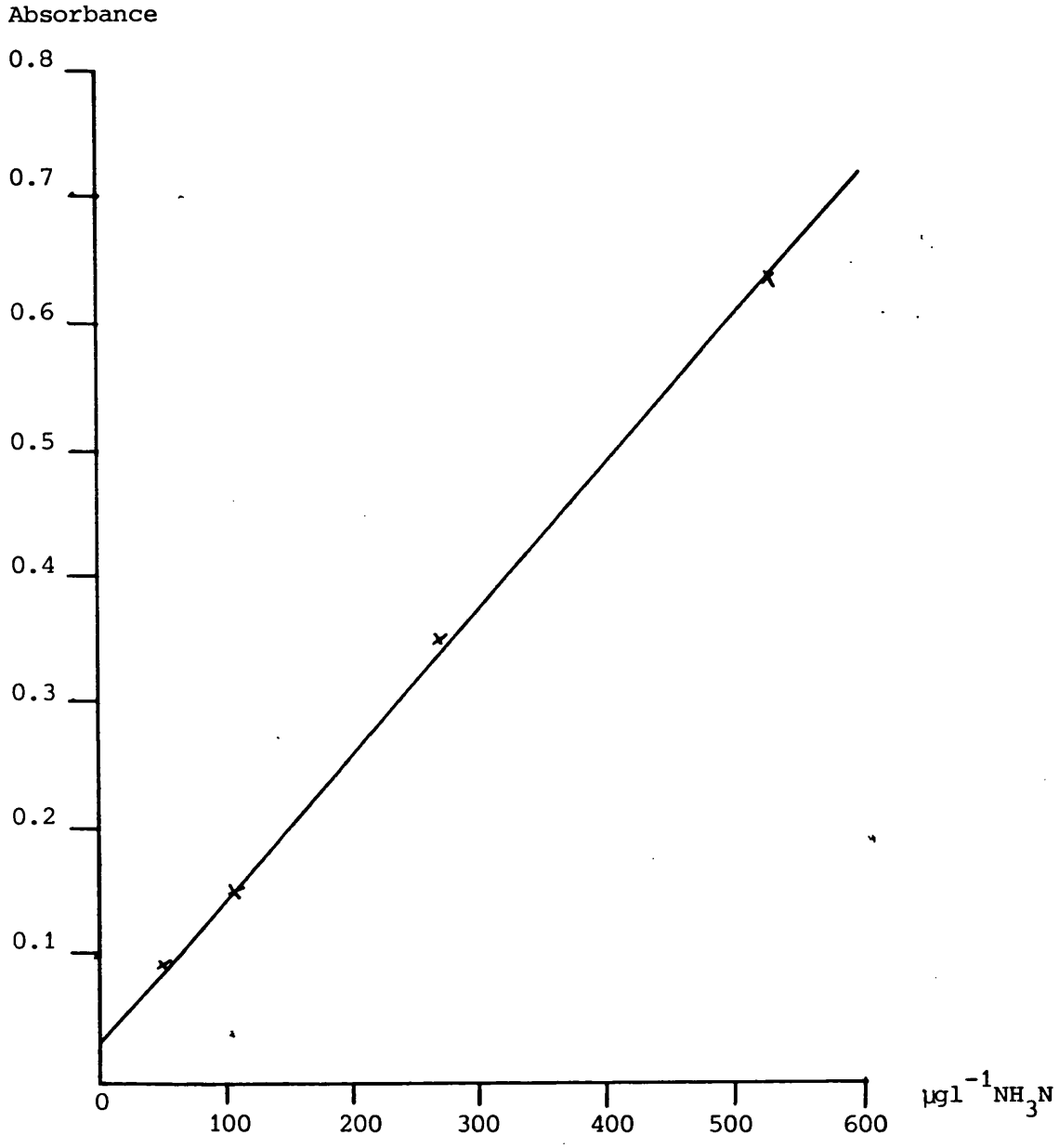
Hydroxylamine is an unstable intermediate in the reduction of nitrogen to ammonia. Determination of hydroxylamine in sea waters has been made with a sensitivity of 0.02µg NH_2OHl^{-1}, but H_2S interferes with this procedure and would, therefore, not be suited to anoxic groundwaters. NH_2OH has been determined in lake waters[182,183].

2.2.8 THE ANALYSIS FOR HYDROXYLAMINE EXPERIMENTAL

A gravimetric determination[182] for hydroxylamine was followed where nickel was complexed in substitution for NH_2OH. The method was sensitive to 0.3mg NH_2OH^-/l.

2.2.8.1 Reagent

Nickel reagent. 5.55g of $NiSO_4 \cdot 7H_2O$ were dissolved in $8cm^3$ of water, and concentrated ammonia solution was added until a deep clear blue colour was obtained. It was then diluted to $300cm^3$. 4g of diacetylmoxine was dissolved in $25cm^3$ of water and added to the nickel solution. 1M NaoH was added until the supernatent turned a greenish yellow. It was allowed to stand overnight in the refrigerator before $10cm^3$ of 1M KOH were added. The solution was filtered to remove the nickel dimethylglyoximate precipitate.



(NB Calibration line does not pass through origin due to contamination with ammonia of the reagents, distilled water or atmosphere)

FIGURE 2.8 THE AMMONIUM CALIBRATION CURVE

2.2.8.2 Procedure

5cm^3 of prepared nickel reagent were added dropwise to 500cm^3 of filtered water sample. The mixture was allowed to stand for 5 hours before filtration through a No 3 porosity sintered glass crucible. The crucible was washed with cold distilled water. The complex was dissolved in a minimum of concentrated HCl, and the solution collected in a small beaker. The filter was again washed with 45cm^3 of distilled water. 1g of ammonium tartrate was added to the solution, which was warmed. The pH was adjusted to 8.5 by addition of ammonia solution. Then a 1% solution of dimethylglyoxime dissolved in methylated spirits was added until complete precipitation occurred. The precipitate mixture was simmered in a water bath for 15 minutes, cooled and filtered through a No 3 porosity sintered glass crucible that had been previously dried at 120°C and weighed. The crucible and precipitate were washed with cold distilled water. It was dried at 120°C, cooled and then weighed. 2M of hydroxylamine were equivalent to 1M of complex having a gravimetric factor of 0.2286.

2.2.8.3 Experimental Results

The method was applied to waters from the Lincolnshire Limestone but the results were inconclusive. Interference from dissolved ions may have accounted for this, for a precipitate of calcium tartrate was formed in some of the samples.

2.3 MICROBIOLOGICAL SURVEY

2.3.1 FIELD PROCEDURES

To determine the population and species of bacteria in aquifer

water, a microbiological survey was carried out at selected field sites.

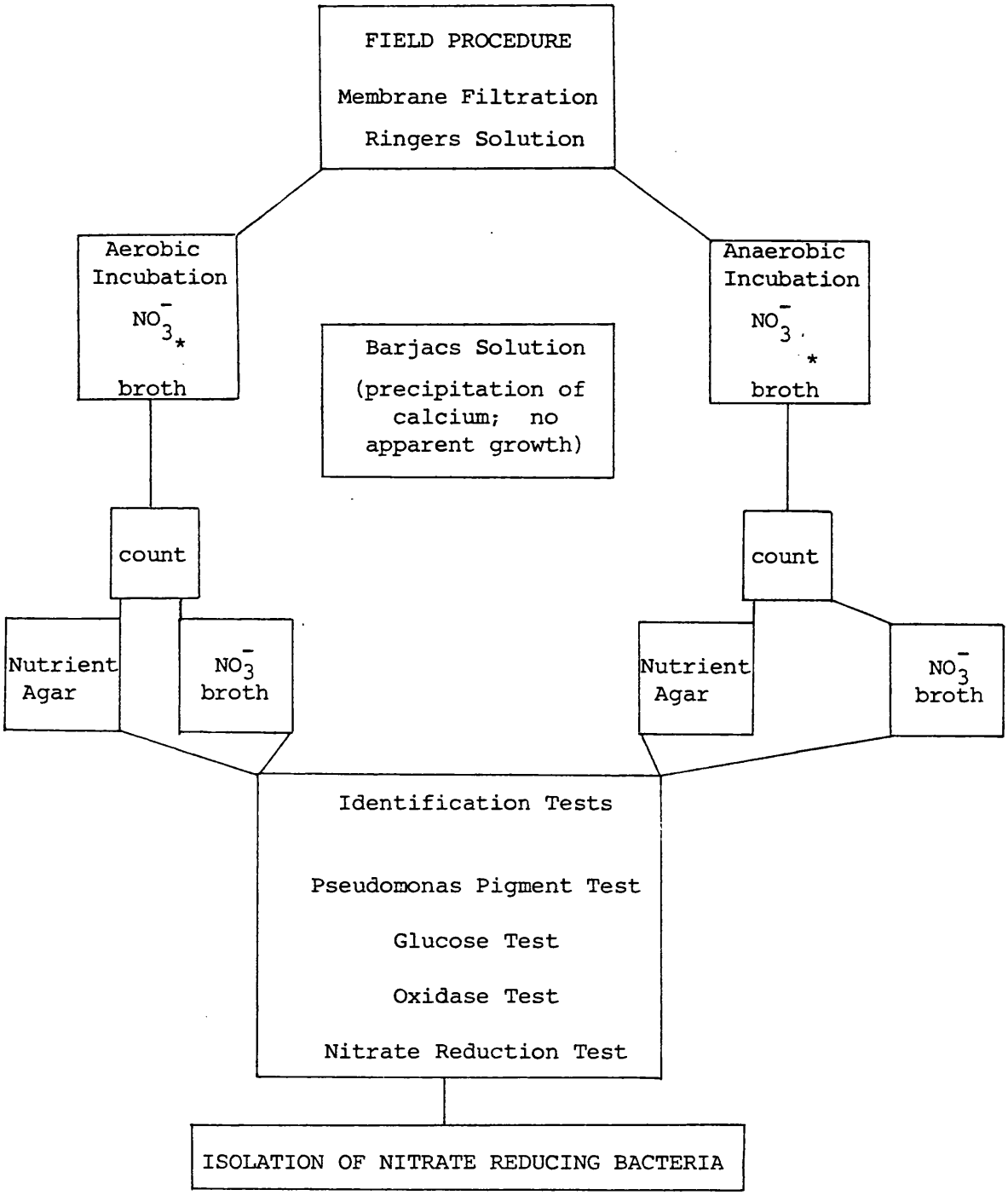
A summary of the procedure is given in figure 2.9 . One litre of water was filtered through a 47mm, 0.2μm Nuclepore polycarbonate membrane. This was supported on either a Millipore inline filter (XX4304700) or a Millipore 'Swinnex' (SX0004700) holder attached to a pumping chamber (figure 2.10).

The filter membrane was transferred, in a sterile field kit (Table 2.6), with tweezers to a universal bottle containing $10cm^3$ of quarter strength Ringers solution. Vigorous shaking dislodged the organisms into the medium. With a Pasteur pipette, four drops of the suspension were made on each of two nitrate broth agar plates[184]. The drops were smoothed over the agar surface with plate spreaders; this ensured even growth. $1cm^3$ of the suspension was added to a universal bottle containing a nutrient solution[185]. One inoculated plate was transferred to an incubation box, and the other plate was sealed in an anaerobic jar. The nutrient solution was placed in an insulated box with cooling packs to limit growth.

2.3.2 BACTERIA IDENTIFICATION PROCEDURES

The samples were incubated at 20°C for seven days. The bacterial populations were then determined. Each agar plate was divided into quarters, and the bacteria in one quarter were counted, so that an estimate of the whole population could be obtained.

The bacteria were described; the colonies at a magnification of 1.25 and the detailed morphology at X1000. Gram stains were performed. All the information for identification was entered on a form.



* 184

FIGURE 2.9 DETERMINATION OF NITRATE REDUCING BACTERIA

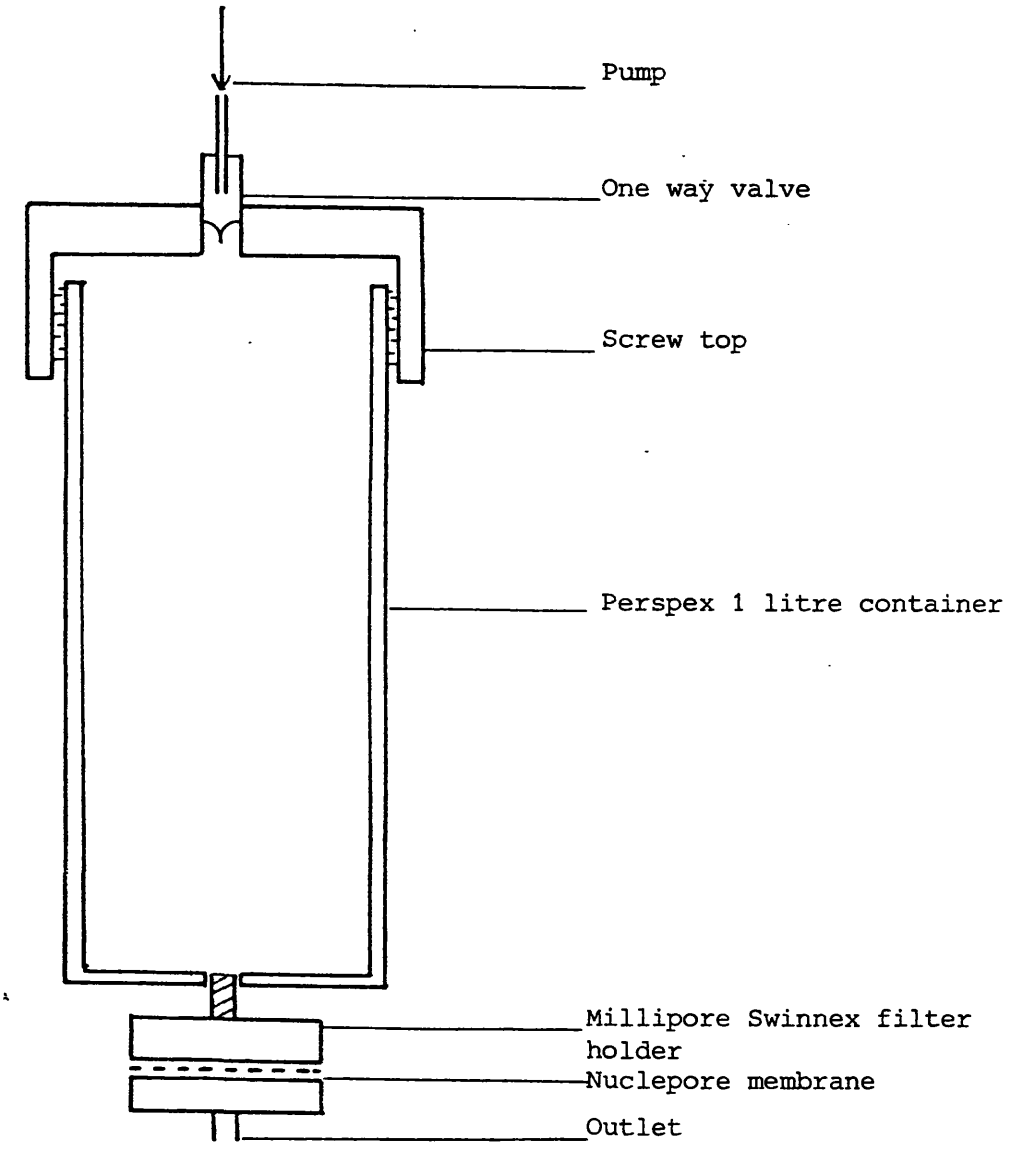


FIGURE 2.10 A PRESSURIZED FILTER ASSEMBLY

TABLE 2.6 A FIELD MICROBIOLOGY SURVEY KIT

One small box containing a sterile autoclavable bag sealed with a wire tag.

The contents of the bag consisted of presterilized equipment:

2 petri dishes with Nitrate broth

1 universal bottle with 10ml $\frac{1}{4}$ strength Ringers solution

1 universal bottle with 10ml Barjac solution

2 pipettes packed in test tubes

1 pair of tweezers

1 spreader

1 glass petri dish containing 4 x 0.22µM Millipore membrane filters and pre-filters.

Further identification tests were necessary. For each bacterial type, two agar slopes were inoculated. One slope was composed of a nitrate broth[184] and the other was nutrient agar. The slopes were then incubated at 20°C to test which species required NO_3^- for growth. Tests were also performed to identify the different genera of bacteria. A pseudomonas pigment test[186] was made to determine the fluorescing species of pseudomonas. A glucose test[187] identified fermentative and oxidative types of metabolism. Pseudomonas species were also differentiated by an oxidase reaction[188]. The bacteria capable of reducing NO_3^- to NO_2^- and other nitrogen oxides, were distinguished[189].

2.3.3 MICROBIOLOGICAL SURVEY RESULTS

A microbiological survey was undertaken on the Lincolnshire Limestone aquifer. The results and conclusions will be further discussed with the chemical analyses (figure 5.4). Three denitrifying bacteria were identified

Pseudomonas indinium

Chromobacterium violateum

Bacillus cereus v mycoides

Fresh cultures of the identified nitrate reducing bacteria were made, and stored in a cool cupboard. Using these cultures it was hoped that denitrification experiments would be carried out to determine the effect of nitrogen isotope fractionation by micro-organisms.

3. INERT GAS AND NITROGEN/ARGON RATIO ANALYSIS

3.1 INTRODUCTION AND LITERATURE REVIEW

Molecular nitrogen is the major product of the denitrification process. To determine the low concentrations of N_2 dissolved in groundwater an analytical procedure capable of recording 1.45 x 10^{-2} cm^3 per cm^3 of water, the solubility of N_2 at S.T.P., to within ±3% was sought.

In early work on dissolved gases in seawater, the N_2 concentration was determined volumetrically[190-191]. Gas chromatography was used to determine the N_2 and Ar contents of seawater to within ±0.5%[192]. A preliminary gas stripping method before chromatographic analysis was used to determine the gas contents of seawater[193,194], and pore water in sediments[195a]. N_2/Ar ratios were detected by difference thermal conductivity with a precision of 2σ = ±0.2%[196].

Mass spectrometry, the most accurate method for gas analysis was used to determine the N_2/Ar ratio on extracted gas samples for aerobic[52] and anaerobic[147] seawater, with a precision of ±1%. The N_2/Ar ratio for groundwater has been measured by a similar method to an accuracy of ±3%.

In this study various methods were tried in order to reach the measurement precision objective. The development can be concisely traced in Figure 3.1, and a detailed account of the experiments follows.

METHOD	ADVANTAGES	PRECISION FOR N_2/Ar	FAULTS AND REASONS FOR DISCONTINUATION
INITIAL PREMISE - THAT MASS SPECTROMETRY WAS THE MOST SUITABLE ANALYTICAL METHOD			
S.I.D.A. using MS.10	Small sample size; existing equipment; good Ar precision.	σ = 0.031 for atmospheric air	Instability in mass spectrometer ion current due to small sample volume of gas used with the static inlet system. Also adsoroption on grease and glass surfaces.
S.I.D.A. using Micromass 602E	Continuous leak inlet; Double collector.	Not determined	Contamination of calibration tracer.
ALTERNATIVE ANALYTICAL METHODS WERE INVESTIGATED ▽			
Gas chromatography	Small sample size using inert gas sample tubes; simple instrumentation.	Not determined	Poor instrumentation which was incapable of distinguishing the argon peak.
Pressure measurement of extracted gases using a McLeod Gauge	Gas extracted directly and measured in the same apparatus	σ = 10.16	Contamination of the getters and mercury with water vapour causing the formation of surface hydroxides.
ALTERNATIVE SAMPLING METHODS WERE INVESTIGATED ▽			
Extraction of gases in evacuated sample bottles.	Sample taken at ambient temperature; no preparation step; concentration of sample on charcoal enables a high pressure to be maintained and therefore less risk of contamination	Manual Mode σ = 13.73 Automatic Mode σ = 2.32	This method reached the required analytical precision and proved suitable for analysis of dissolved nitrogen in groundwater.

FIGURE 3.1 A FLOW DIAGRAM OF THE METHODS USED TO DETERMINE THE N_2/Ar RATIO

3.2 STABLE ISOTOPE DILUTION ANALYSIS (S.I.D.A.)

Stable Isotope Dilution Analysis was used to analyse the small quantity of gas extracted from a 1-2cm^3 sample of ground water. The basic principle depends on the sample of gas being diluted by a gas of a known volume and isotopic composition. After equilibrium, the isotopic ratio of the mixture is determined and so the composition and concentration of the original gas can be calculated.

3.2.1 INERT GAS ANALYSIS USING S.I.D.A. ON THE MS.10

Gases dissolved in groundwaters are predominantly of atmospheric origin. Helium is used to date waters[158] and Ar, Kr and Xe can be used as paleotemperature indicators[135]. The technique was extended to the determination of the N_2/Ar ratio.

3.2.2 INERT GAS ANALYSIS USING S.I.D.A. - EXPERIMENTAL

3.2.2.1 Apparatus

A glass preparation line was built (figure 3.2) to extract the dissolved gases from the water under vacuum. After a process of separation the gases were analysed using a Kratos MS.10 mass spectrometer with a 2in radius, 180° magnetic deflection and single collector.

3.2.2.2 Procedure

A gas sample tube (figure 3.3) containing 1-2cm^3 of water was attached to the evacuated glass preparation line. The line was pumped

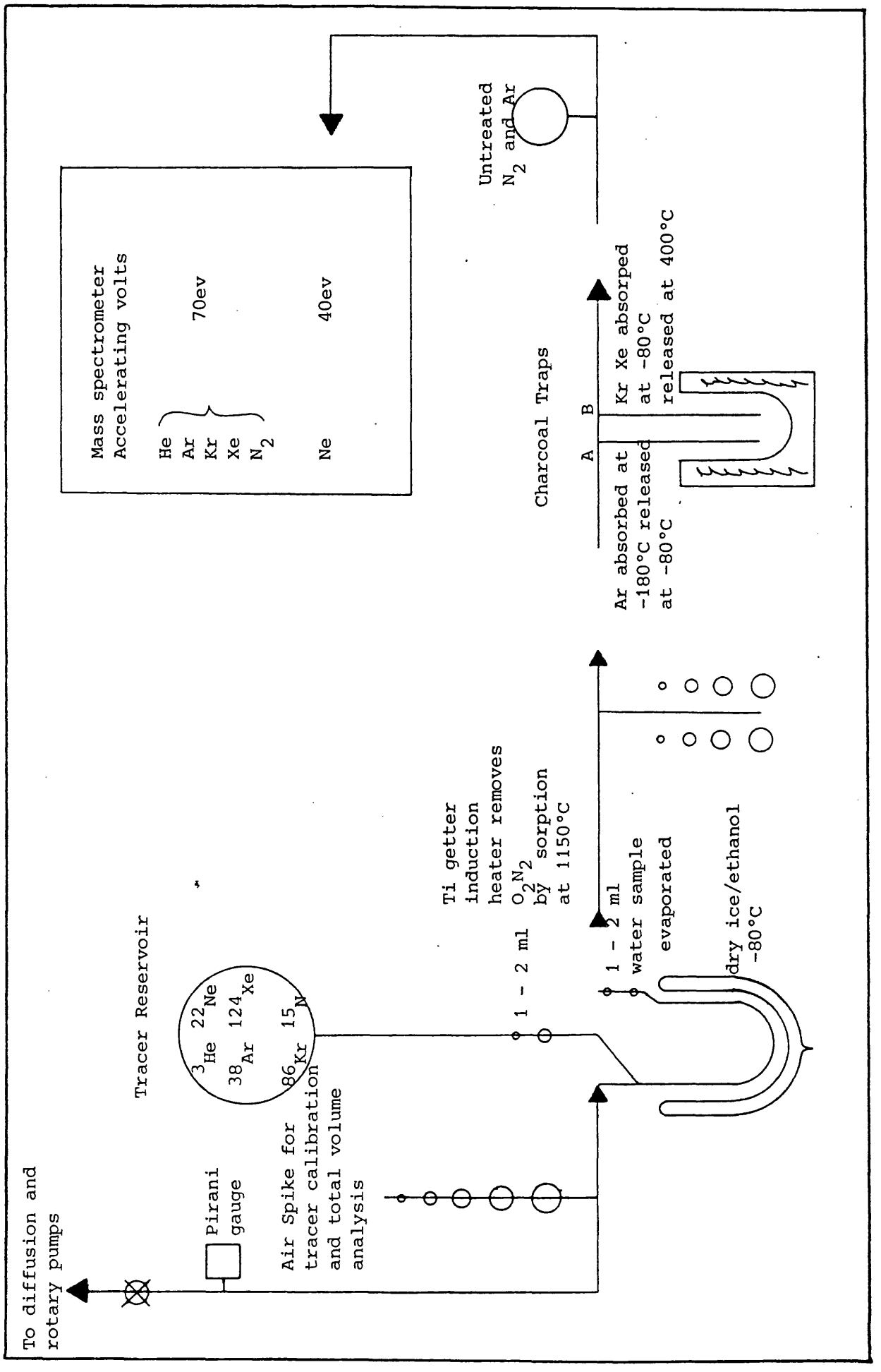


FIGURE 3.2 INERT GAS EXTRACTION LINE

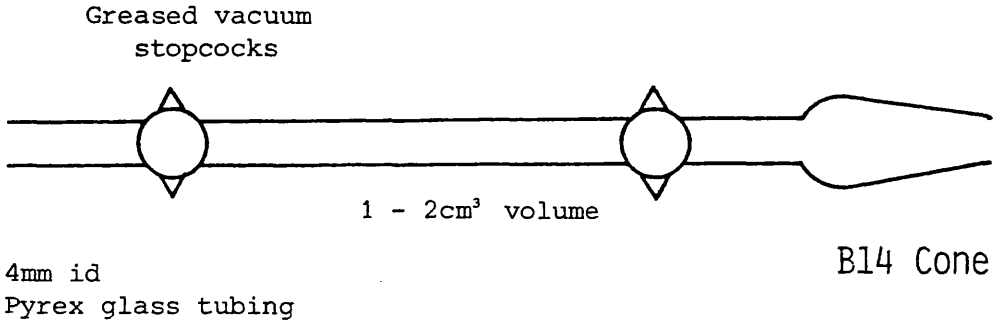


FIGURE 3.3 AN INERT GAS SAMPLE COLLECTION TUBE

to a vacuum of better than 10^{-5} torr. The titanium getter was cleaned by cycles of heating and pumping. The charcoal traps were baked to 450°C and pumped whilst cooling. The taps to the pumps and charcoal traps were then closed. A dry ice/alcohol bath was used to cool the charcoal. A volume of tracer gas, enriched with the rare isotopes of the inert gases and $^{15}N_2$ was metered into the line. A water sample was admitted to the preparation line, vaporised in an inlet system, and then dried with a dry ice/alcohol mixture. A portion of the gas was trapped in a bulb for subsequent N_2/Ar analysis. O_2 and the remaining N_2 were removed by Ti gettering. Charcoal trap B (figure 3.2) was opened for 10 min at -80°C to absorb Kr and Xe, then closed. Liquid nitrogen was placed around trap A and the tap was opened and then closed after 10 mins, to remove Ar from the system.

He and Ne were admitted to the mass spectrometer for analysis. He was measured at 70V electron accelerating potential whereas Ne was measured at 40V. ^{40}Ar and $^{20}Ne^+$ have a similar charge/mass ratios but $^{40}Ar^{2+}$ cannot be ionized at the lower accelerating potential, thus avoiding erroneous peak heights.

The preparation line was pumped clean before Ar was released from charcoal trap A. The gas was cleaned by gettering and analysed. The preparation line was again pumped down, and the trap B opened and pumped for 30 seconds. The trap was closed, and the coolant exchanged for a furnace, which was heated to 450°C. The getter was cleaned again, and the pumps were closed. After 10 minutes heating the Kr/Xe trap was opened and closed; the getter was heated and cooled completely before admitting the released gases (Kr and Xe) for analysis.

The preparation line was pumped down again in readiness for the isolated nitrogen and argon sample. The gas was admitted to the mass spectrometer at a suitably adjusted pressure. The gas was not trapped on the charcoal since it caused fractionation of the nitrogen isotopes at low gas concentrations. (Table 3.1). The preparation line was then pumped and the charcoal traps and getter cleaned in readiness for the next sample.

3.2.2.3 Calculation of Results

The ratio of the gases were then calculated from the equation:

$$R = \frac{^{38}Ar}{^{40}Ar} = \frac{^{38}x \text{ at } Vat\ (Ar) + {}^{38}xt\ Vt(Ar)}{^{40}x \text{ at } Vat\ (Ar) + {}^{40}xt\ Vt(Ar)}$$

where:

V at (Ar) = volume of atmospheric argon at S.T.P.

Vt (Ar) = volume of tracer argon at S.T.P.

$^{\infty}x$ at = mole fraction of isotope $^{\infty}Ar$ in atmospheric Ar

$^{\infty}xt$ = mole fraction of isotope $^{\infty}Ar$ in tracer Ar

If Vt, and the isotopic composition of the tracer and the atmospheric inert gases are known, Vat may be calculated once the ratio R has been determined experimentally.

$$V \text{ at } (Ar) = V_t(Ar).\frac{(^{38}xt - {}^{40}xt.R)}{(^{40}x \text{ at } R - {}^{38}xat)}$$

In practice the tracer spike volume Vt was determined first by mixing with a known volume of atmospheric inert gas from a metered volume of air. The calculation of the tracer ratio was completed on a computer using the program AIRCAL (Appendix C). The tracer composition was corrected using a

TABLE 3.1 THE FRACTIONATION OF NITROGEN ISOTOPES ON CHARCOAL

MASS UNITS	28	29	30	RATIO 30/28
	Ion currents in arbitrary units			
SAMPLE Complete Tracer	795	218	289	2.111
After being trapped on charcoal for 10 minutes	193	198	239	0.818

standard of air equilibrated distilled water, and the calculations were made using a program WATCAL (AppendixC). The gas composition and N_2/Ar ratio were computed using the program GASAN (Appendix C).

3.2.2.4 Calibration Results, Precision and Accuracy

The analysis of argon gave reproducible results for $^{15}N/^{14}N/Ar^{40}$ ratio with a precision of $\sigma \doteq 0.1$. Determination of the nitrogen isotope ratio 29/28 for atmospheric air could be measure with a σn of 0.0001 and an accuracy of ±2%.

The measurement of 0.3552 for the 29/40 ratio for atmospheric air has a precision of $\sigma = 0.031$, but the accuracy was poor differing significantly from the theoretical value of 0.6084 (Table 3.2).

The poor N_2/Ar ratio measurement for atmospheric air could be explained by a large difference in the concentrations of the gases, and the different sensitivities in the system for N_2 and Ar. Oxygen was not removed, so NO may have formed and contaminated the sample gas too. The ion current for nitrogen declined rapidly[195] with the static inlet system. Exchange of N_2 for gases adsorped on the surface of the glass preparation line, and Apiezon N grease was known to alter the isotopic composition[192].

The results are given (Table 3.3) for N_2/Ar volumetric determination using air saturated distilled water. The observed variation was unsatisfactory and so this method, using a static inlet mass spectrometer and S.I.D.A. was discontinued.

TABLE 3.2 DETERMINATION OF MASS 29/28 ($^{15}N^{14}N/^{14}N_2$) RATIO AND MASS 29/40 ($^{15}N^{14}N/^{40}Ar$) RATIO USING AN MS.10 MASS SPECTROMETER

SAMPLE	RATIO 29/28	σ	RATIO 29/40	σ
Air Spike 1	0.0076	0.0001	0.3552	0.001
Air Spike 2	0.0076	0.0001	0.3440	0.001
Air Spike 3	0.0076	0.0001	0.3239	0.001
Air Spike 4	0.0075	0.0001	0.3976	0.016
		RATIO 29/40	MEAN 0.3552	σ 0.031

TABLE 3.3 VOLUMES OF DISSOLVED NITROGEN AND ARGON IN DISTILLED WATER SAMPLES DETERMINED BY S.I.D.A. ON THE MS.10 MASS SPECTROMETER

	N_2 cm^3/cm^3 H_2O	Ar cm^3/cm^3 H_2O	N_2/Ar
1.	4.538×10^{-3}	7.454×10^{-3}	0.609
2.	4.375×10^{-3}	3.404×10^{-3}	1.285
3.	0.134	0.022	6.091
4.	0.142	0.02	7.1
5.	0.136	1.079×10^{-4}	1236.36
6.	0.014		
7.	0.164		
8.	0.058		
9.	0.089		
10.	0.080		
11.	0.103		
12.	0.088		
13.	0.058		

3.2.3 N_2/Ar DETERMINATION USING S.I.D.A. ON A MICROMASS 602E

By using a mass spectrometer with a continuous leak inlet system, the problem of a decreasing Nitrogen ion current was eliminated. Argon could still be more accurately determined on the MS.10.

A separation line was built, designed to add tracer gas to the sample. The tracer was composed of $^{15}N_2$ (95 Atom %) and ^{36}Ar (99.5 Atom %). The gases were mixed at a pressure of approximately 100 torr. Measurement of the tracer ratio could not be precisely resolved, as shown by the erratic results given in Table 3.4. The error was attributed to leakage of atmospheric air into the tracer storage container. The tracer was the only means of cross calibrating the MS.10 with the Micromass 602E mass spectrometer. Only one measurement came within 1%. Therefore, since the isotopic ratio of the tracer could not be determined, the measurement of N_2/Ar by this procedure was discontinued.

3.3 DETERMINATION OF THE N_2/Ar RATIO BY GAS CHROMATOGRAPHY

3.3.1 A REVIEW OF N_2/Ar ANALYSIS BY GAS CHROMATOGRAPHY

Dissolved gas concentrations of N_2 and Ar to within 0.3ppm in 1-2cm^3 samples of seawater have been determined using a gas stripping chamber[197]. The extraction method has been used on groundwaters[198] and sediment pore waters[193]. By increasing the length of the chamber, larger samples can be treated. Continuous stripping methods have also been developed[199,206].

Conservative gases needed to be separated from a wet medium, and

TABLE 3.4 DETERMINATIONS OF ^{36}Ar AND ^{15}N IN THE TRACER PREPARED FOR S.I.D.A. USING THE 602E MASS SPECTROMETER

	RATIO 36/40		RATIO 28/30
	MS.10	602E	602E
1.	47.89		1.557
2.	16.215		
3.			7.598
4.	24.739		
5.	4.79	4.762	0.4812*
6.	4.77		
7.		0.218	0.5175*
8.		0.214	0.5009*
9.			0.5087*
10.	27.45*		
11.	23.79*		
12.	23.26*		
13.	24.74*		
	Mole fractions		Mole fractions
	^{40}Ar = 3.528		$^{30}N_2$ = 66.64
	^{36}Ar = 96.472		$^{28}N_2$ = 32.36

* Values used to calculate mole fractions

this limited the choice of chromatography column packs. Low polarity polymers with moderate absolute retentions are recommended[201]. Columns such as Poropak and Chromosorb give good separation, but the 5A° Molecular sieve, especially below ambient temperatures has been most widely used [192, 202-204]. The difficulty of distinguishing Ar from O_2 was acknowledged and a catalytic conversion process using palladium to remove O_2 in the form H_2O was used[137].

Essential to the stripping method was the assumption that equilibrium had been reached between the bubbles of the carrier gas in the stripping chamber, and the gases in solution. The stripping process follows a simple first-order Rayleigh curve. The characteristic time t_i, required to reduce the concentration of the gas i in solution by the factor 1/e is given by

$$t_i = \frac{\beta i \; Vl \; P}{F}$$

where:

βi = Bunsen solubility of the gas i at the temperature of the liquid

Vl = Volume of the liquid

F = Volume flow rate of the carrier gas at S.T.P.

P = The pressure inside the stripper in atmospheres.

The equation gives the characteristic extraction time for the liquid phase, therefore, the flushing time for the mixed gas volume above the liquid inside the stripper is

$$V/F$$

where V is the volume of gas and F is the volume flow rate at the stripper temperature and pressure[137]. Thus the characteristic stripping time

for each gas is proportional to its solubility in the liquid phase.

3.3.2 THE ANALYSIS FOR N_2/Ar BY GAS CHROMATOGRAPHY - EXPERIMENTAL

3.3.2.1 Apparatus

A gas extraction line was designed (figure 3.4) to strip and analyse the dissolved gases from a 1-2cm³ water sample. An all Pyrex stripping chamber was made[197,199] with a coarse fritted glass disc at the base (figure 3.5). The sample was introduced from a glass sample tube (figure 3.3), A capillary U-tube was connected to the stripping chamber to dry the extracted gases by freezing, before entry to the chromatographic column.

A 72in by 0.25in stainless steel separation column was packed with 5A° Molecular sieve, mesh 30-60[137]. A Perkin Elmer thermal conductivity cell, containing four thermistor detectors was controlled by a Gas Chromatography Katharometer detector Type 1E (Patt Appl No: 32999/64) console. The output signal from the detectors was recorded in a 1mV Honeywell recorder, with a chart speed of 15in per minute.

Helium was used as the carrier gas at a flow rate of 50cm³ min. The gas flow was measured with a soap bubble flowmeter, and a rotameter.

3.3.2.2 Procedure

The whole system was flushed with carrier gas for 30 minutes. The 3-Way Teflon valve and toggle valve were turned so that the sample chamber was by-passed. The stripping chamber was evacuated to approximately 10^{-2} torr and then the sample was admitted. Then the carrier supply was rerouted so that it bubbled through the sample, stripping the dissolved gases out of solution.

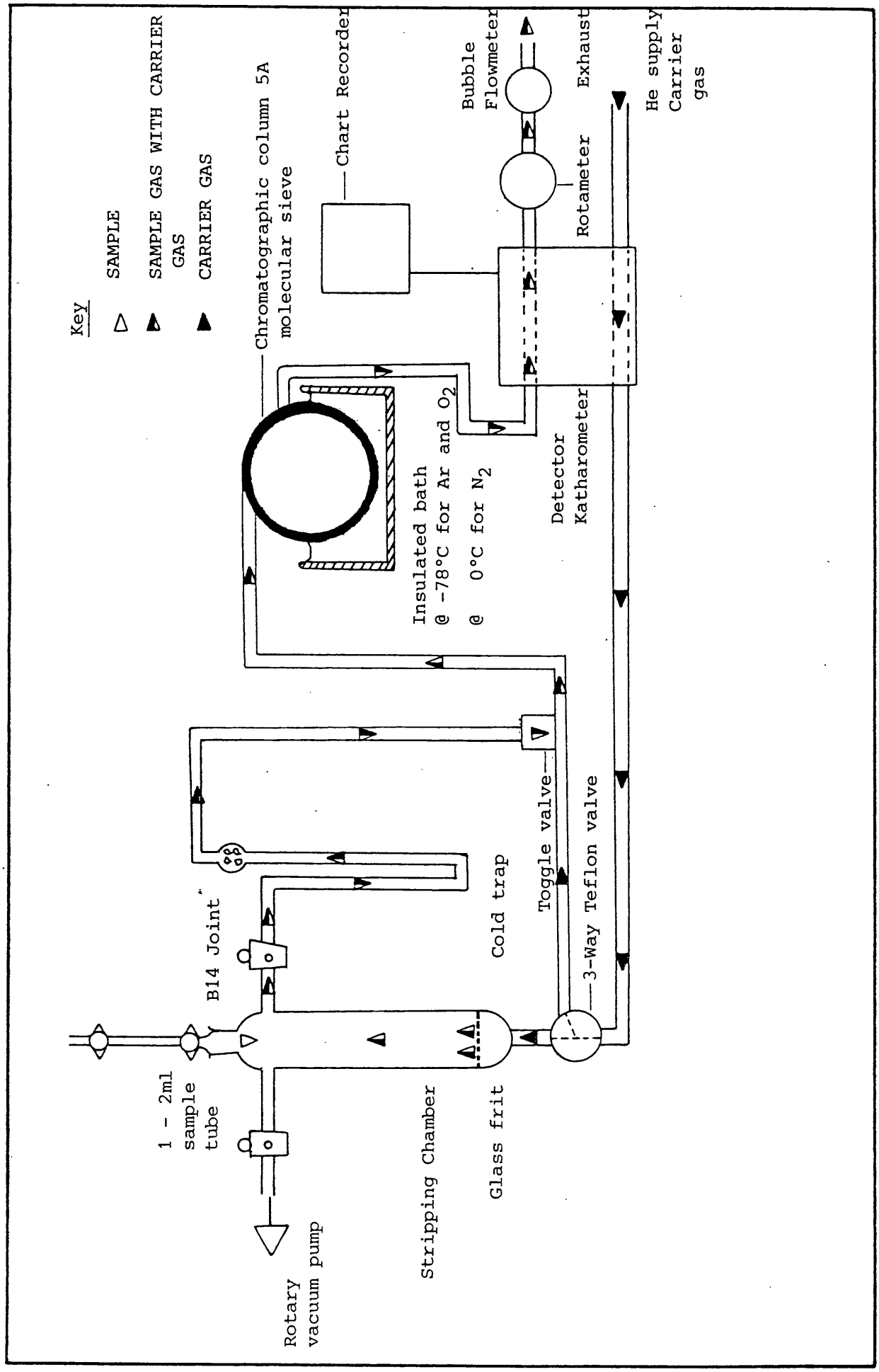


FIGURE 3.4 APPARATUS FOR GAS CHROMATOGRAPHIC ANALYSIS

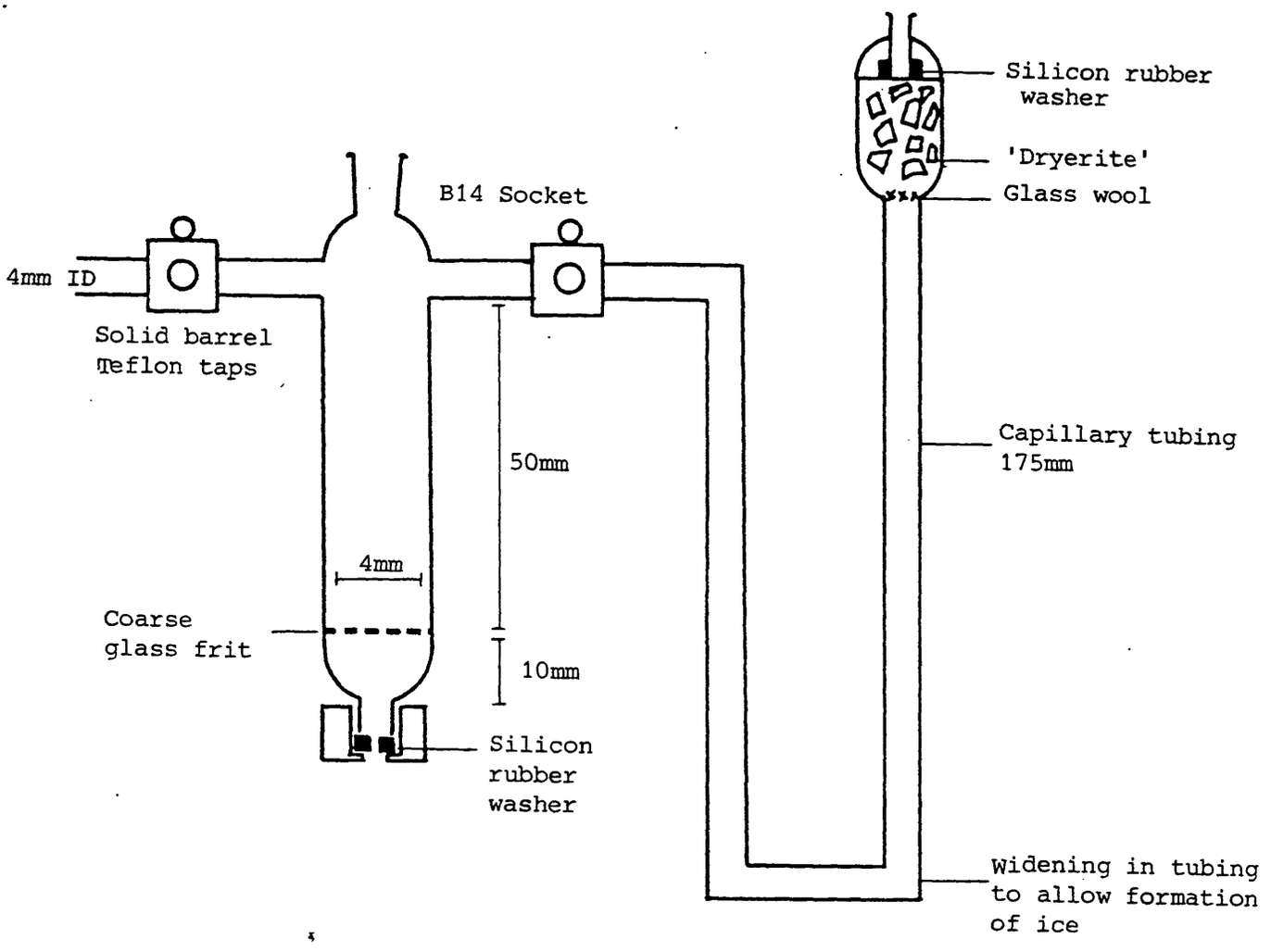


FIGURE 3.5 A STRIPPING CHAMBER FOR DEGASSING WATER BEFORE GAS CHROMATOGRAPHIC ANALYSIS

The carrier gas and entrained extracted gases were dried at -78°C in the cold trap 'Dryerite' was packed into the top of the trap to adsorb the last traces of moisture.

Ar was eluted after 5 minutes on passing through the 5A° molecular sieve column at -78°C and 0_2 was eluted 2 minutes later. Nitrogen remained on the column until the refrigerant was exchanged 9 minutes later for an ice bath at 0°C. After a further 3 minutes nitrogen was eluted.

After each analysis the stripping chamber was cleaned. Once re-assembled, the extraction line was flushed with carrier gas for 15 minutes before the admission of the next sample.

3.3.2.3 Results, Precision and Accuracy

To calibrate the system approximately 1.5cm^3 of air was injected, but the argon peak could not be detected with this large volume. The resolution of the detector was proved to be insufficient for this experiment. Since no other equipment was available this method of analysis was discontinued.

3.4 VOLUMETRIC DETERMINATION OF N_2/Ar USING A MCLEOD GAUGE

The principle of the McLeod gauge was first described by McLeod in 1874. By compressing a given volume, V, of gas to a much smaller volume, v, the resultant pressure p can be measured. Then in accordance with Boyle's Law, the original pressure P can be calculated from

$$P = \frac{p.v}{V}$$

3.4.1 EXPERIMENTAL

The dissolved gas was extracted from a $5cm^3$ water sample. It was admitted to a preparation line where, by exposure to a Mg mirror getter, oxygen and gaseous oxides were removed. Then the pressure of the remaining gases, comprising nitrogen and the inert gases was measured with a McLeod gauge. The sample gas was further treated by operating a Ti getter to remove the nitrogen. The pressure of the remaining inert gases, principally composed of argon, was again measured with a McLeod gauge. The total volume of the N_2 and Ar in the sample was calculated by difference and an N_2/Ar ratio obtained.

3.4.1.1 Apparatus

A vacuum preparation line was designed (figure 3.6) incorporating a McLeod gauge. The borosilicate glass furnace tube, containing Mg turnings was operated at 450°C and the quartz glass furnace tube containing Titanium sponge (>600μ, mesh 25; >99.9%) was operated at 800°C.

The McLeod gauge was constructed of two diameters of capillary tubing. The larger lower tube 'A' of diameter 2.0mm measured the pressure of the nitrogen and the upper capillary 'a' of diameter 0.5mm measured the pressure of the inert gases. A bulb of 0.6485 cm^3 was incorporated between the two capillaries and enabled the accommodation of the large pressure difference between nitrogen and argon. The capillary series was attached to a large bulb 'B' and then to a barometric column and mercury filled reservoir.

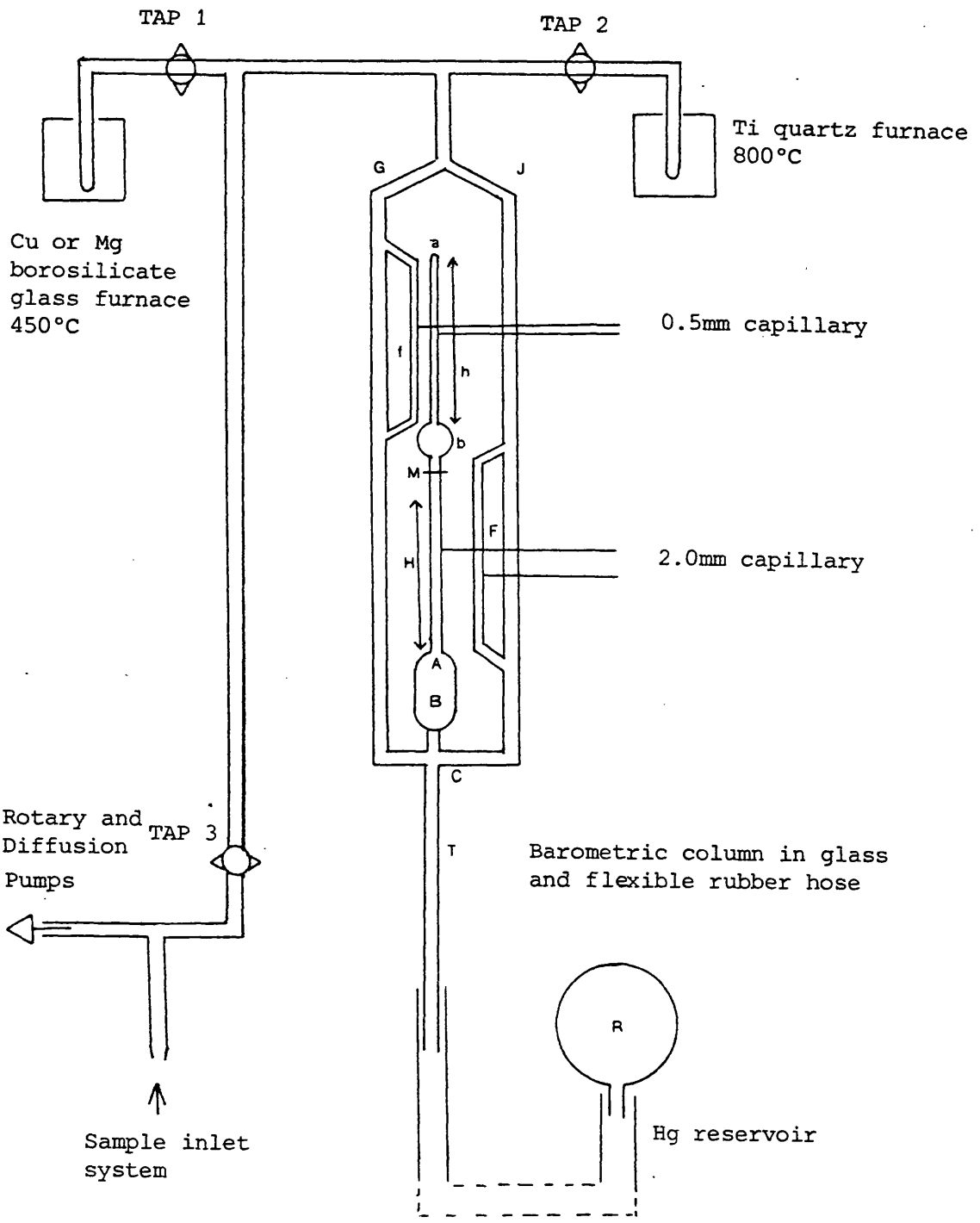


FIGURE 3.6 THE VACUUM PREPARATION LINE AND MCLEOD GAUGE

3.4.1.2 Procedure

The preparation line was evacuated to better than 10^{-4} mb. 0.2g Mg turnings were heated to just above 443°C, at which temperature the metal sublimes to form a mirror on the furnace tube walls. The furnace was cooled before tap 1 was closed. The Ti sponge was cleaned by heating and pumping and then allowed to cool before taps 2 and 3 were closed.

A $5cm^3$ glass gas sample tube was attached to an inlet system. The line was evacuated and the dissolved gases from the water sample extracted by a process of evaporation and freezing of the moisture vapour. Tap 3 was opened and the gas sample admitted to the preparation line. Tap 1 was opened and oxygen and gaseous oxides were absorbed on the magnesium mirror

$$2Mg^{++} + O_2 \rightarrow MgO$$

The pressure of the remaining gases, nitrogen and the inert gases was measured. The Ti getter was heated to 800°C and cooled before the pressure of Ar was measured. The getters were cleaned by heating and pumping. The whole system was then pumped for 30 minutes in preparation for the next sample.

3.4.1.3 Calculation of Results

The volumes of gases were calculated from the pressure readings as follows:

To calculate the volume of Nitrogen:

Volume measured = b + a + (M-H)D

$$\text{Pressure of the system} = \frac{P_{\text{measured}} \times V_{\text{measured}}}{V_{\text{gauge}}}$$

$$\text{Volume of nitrogen gas at STP} = \frac{P_{\text{system}} \times V_{\text{system}}}{P_{760}}$$

To calculate the volume of argon:

$$\text{Pressure of the system} = \frac{dh^2}{[(B+b+A) - dh]}$$

$$\text{Volume of argon gas at STP} = \frac{P_{\text{system}} \times V_{\text{system}}}{P_{760}}$$

where:

B = volume of large bulb

b = volume of small bulb

a = volume of 0.5mm capillary

A = volume of 2.0mm capillary

M = lower edge of black line below $0.5cm^3$ bulb

H = Δ in height of mercury in mm below M

h = Δ in height of mercury column in 0.5mm capillary

D = volume of 2mm capillary per $1cm^3$

d = volume of 0.5mm capillary per $1cm^3$

V system = $287.730cm^3$

V gauge = $144.159cm^3$

A program MCLEOD (Appendix C) was written to calculate the N_2/Ar ratios from the measurement of pressure.

3.4.1.4 Calibration Results

The precision of the McLeod gauge was measured, by the introduction

of an air spike into the preparation line without exposure to the metal getters (Table 3.5). This showed that the gas pressure could be precisely measured with δ_n of 0.042 mmHg.

When the sample gas was exposed to a cold clean Ti getter, the precision fell and the δ_n = 2.03 mmHg (Table 3.6). Determinations of N_2/Ar on air samples showed a poor reproducibility (Table 3.7) of δ_n = 10.16 and the accuracy was ±13%. For water samples the measurements were even less precise. Water vapour contaminated the preparation line, and surface hydroxides formed on the getters. This reduced the active surface area. Water vapour was also trapped in the mercury. Due to this contamination problem and the poor precision of calibration, the method was discontinued.

3.5 THE DETERMINATION OF THE N_2/Ar RATIO FOR SAMPLES COLLECTED IN EVACUATED BOTTLES BY MEASUREMENT OF THE $^{29}N_2/^{40}Ar$ RATIO WITH A MICROMASS 602E MASS SPECTROMETER

A final method was developed which overcame the problems inherent in the techniques discussed previously. Experience showed that four criteria needed to be incorporated:

i) Large sample size of approximately 150cm^3;

ii) Field extraction of the gases reduced the risk of contamination during transportation;

iii) The gas samples prepared for analysis were maintained at or near atmospheric pressure, to prevent contamination;

iv) A diffusive leak, dual collector mass spectrometer operated by computer control was necessary for accurate analysis.

TABLE 3.5 FIVE REPLICATE MEASUREMENTS OF THE PRESSURE OF TWO ATMOSPHERIC AIR SAMPLES USING A McCLEOD GAUGE

SAMPLE	PRESSURE IN mmHg	MEAN	σ
0.1 cm^3 air	53.32 52.92 53.39 54.46 53.43	53.50	0.051
0.1 cm^3 air	53.18 53.06 53.69 53.25 53.93	53.42	0.033
mean for all 10 readings = 53.43 (σ = 0.042)			

TABLE 3.6 PRESSURE MEASUREMENTS, USING A McCLEOD GAUGE, OF ATMOSPHERIC AIR SAMPLES EXPOSED TO THE CLEAN COLD TITANIUM GETTER

SAMPLE	PRESSURE IN mmHg
0.1 cm^3 air	54.81
0.1 cm^3 air	50.42
0.1 cm^3 air	51.63
0.1 cm^3 air	47.72
0.1 cm^3 air	(93.93)
0.1 cm^3 air	49.30
0.1 cm^3 air	50.45
0.1 cm^3 air	51.21
mean for 7 readings	= 50.79 (σ=2.03)

TABLE 3.7 THE MEASUREMENT OF N_2/Ar ON 0.1 cm^3 AIR SAMPLES USING THE MCLEOD GAUGE

N_2/Ar RATIO
89.241
85.085
84.071
77.712
72.852
71.766
64.909
63.274
62.761
58.429
Mean = 73.01 σ = 10.16
The ratio of N_2/Ar in atmospheric air = 83.871. This method has an accuracy of ±13%.

3.5.1 THE DETERMINATION OF N_2/Ar - EXPERIMENTAL

3.5.1.1 Apparatus

The field sample was collected in a 250cm³ glass bottle, with a right angle greased (Apiezon - T) [205] vacuum stopcock (figure 3.7a). The bottle was evacuated to better than 10^{-3} mb and atmospheric contamination by leakage amounted to no more than 0.2% by volume.

To fill the bottle in the field, a device (figure 3.7b) was inserted into the bottle neck. A vacuum preparation line was designed (figure 3.8) for the transfer of sample gas from the 250cm³ bottle to a charcoal trap (figure 4.3).

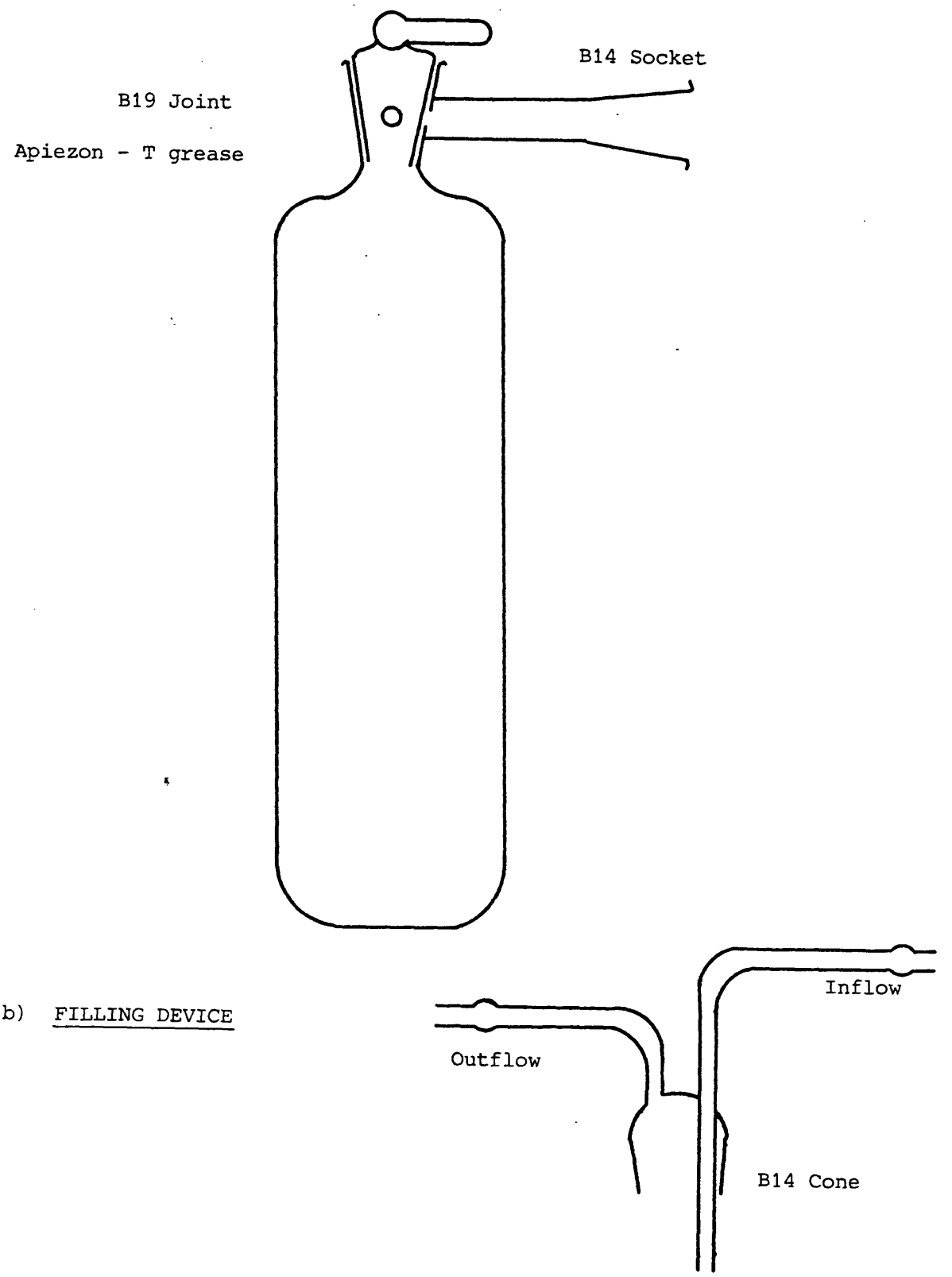
3.5.1.2 Field Procedure

A charcoal trap was attached to the preparation line and cleaned by heating to 400°C and vacuum pumping. It was allowed to cool and then isolated. A sample bottle was attached and the line evacuated. A liquid nitrogen coolant was placed around the charcoal trap, and a dry ice/alcohol trap was placed on the cold finger. The tap of the sample bottle was opened for 10 seconds, producing a system pressure of approximately 200 torr. The gas was dried by freezing for 10 minutes. The charcoal trap was then exposed at -178°C, and the pressure dropped to 3×10^{-1} mb as the gases were adsorbed. The sample was sealed into a charcoal trap for subsequent analysis.

3.5.2 ANALYSIS OF N_2/Ar ON A DUAL COLLECTOR MASS SPECTROMETER

The N_2/Ar was measured by determination of the ion currents of mass 29 and 40. It was assumed that the isotopes of nitrogen were fully equilibrated

a) 250 cm^3 GLASS SAMPLE BOTTLE



b) FILLING DEVICE

FIGURE 3.7 THE EVACUATED SAMPLE BOTTLE AND FILLING DEVICE

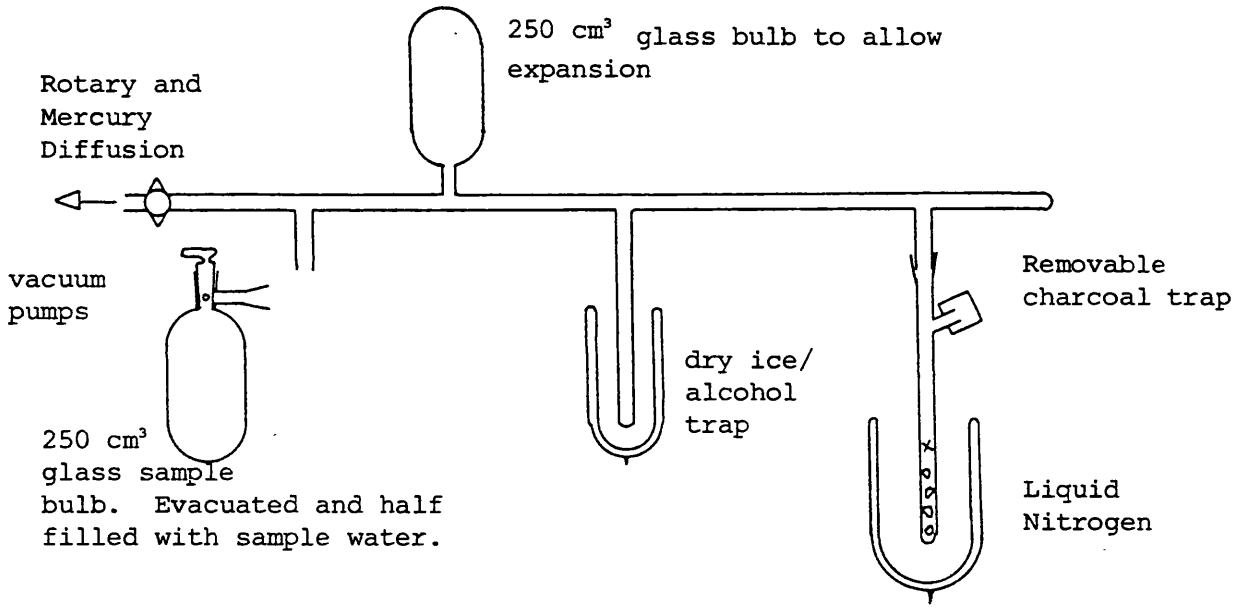


FIGURE 3.8 PREPARATION LINE FOR THE TRANSFERENCE OF GAS FROM THE SAMPLE BOTTLE TO THE CHARCOAL TRAP

amongst the molecular species. For a mixture of p atoms of ^{14}N and q atoms of ^{15}N, the ratio of molecular species is then given by

$$28:29:30 \equiv p^2 : 2pq : q^2$$

The nitrogen/argon volumetric ratio is approximately (within 0.03%) equal to the 28/40 ratio so that

$$N_2/Ar = \frac{28_I}{40_I}$$

where: I's are the ion currents.

provided that no mass discrimination occurs between mass 28 and 40 ions in the mass spectrometer.

The Micromass 602E was initially operated by manual control. The minor amplifier was used as a single collector, but temporal variations of the instrument settings gave poor reproducibility for atmospheric air calibrations. Within a batch of samples, where δ_n = 1.20, the N_2/Ar was enhanced from the theoretical value of 81.884. The between batch analyses were more variable with a δ_n = 12.50 (Table 3.8).

An automatic procedure for tuning the instrument to the accelerating voltage peak maxima and for collection of data was developed[208] (figure 3.9). The mass spectrometer was operated in the dual collector mode with dried atmospheric air as the reference gas. This enabled the determination of both the $^{15}N/^{14}N$ ratio and N_2/Ar ratio to be carried out consecutively and the reproducibility of measurement was improved to δ_n = 0.006 and to within ±0.6% of the theoretical ratio (Table 3.9).

3.5.2.1 Procedure

The sample and reference gases were admitted to the mass spectrometer.

TABLE 3.8 DETERMINATIONS OF N_2/Ar FOR ATMOSPHERIC AIR, ON THE MICROMASS 602E MASS SPECTROMETER, USING THE MINOR AMPLIFIER IN THE SINGLE COLLECTOR MODE

	RATIO 29/40	N_2/Ar	
			'within batch'
1.	0.6225	83.715	n = 5
1.	0.6307	84.541	Mean = 85.685
1.	0.6430	86.541	σ = 1.20
1.	0.6455	86.878	
1.	0.6420	86.406	
2.	0.5005	67.362	
3.	0.5209	70.108	
4.	0.6859	92.314	
5.	0.7139	96.083	
6.	0.7768	104.549	'between batch'
7.	0.5953	80.121	
8.	0.5940	79.946	n = 10
9.	0.6009	80.875	Mean = 85.842
10.	0.7340	98.789	σ = 12.50
11.	0.7331	98.668	
	0.6084	81.884	AIR VALUE

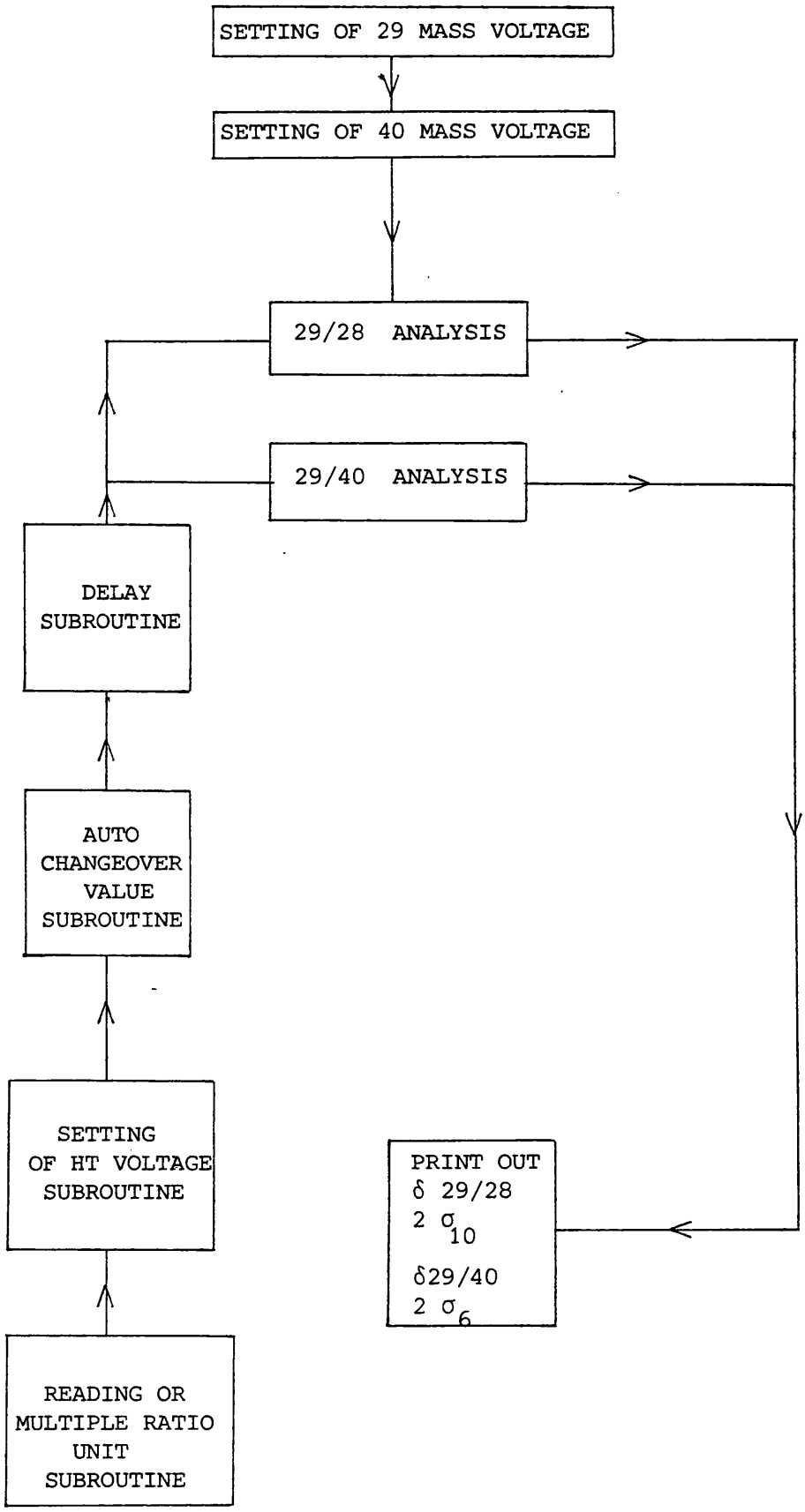


FIGURE 3.9. FLOW DIAGRAM OF THE AUTOMATIC DATA COLLECTION PROGRAM FOR THE MICROMASS 602E MASS SPECTROMETER

TABLE 3.9 TEN CONSECUTIVE MEASUREMENTS OF δ29/28 AND δ29/40 OF A STANDARD AIR SAMPLE RECORDED AUTOMATICALLY

δ29/28 °/oo	$2\sigma_{10}$	δ29/40 °/oo	σ	29:40
-0.09	0.04	6.37	0.21	0.6123
-0.03	0.03	6.19	0.15	0.6122
-0.02	0.05	6.18	0.19	0.6121
-0.04	0.04	6.11	0.25	0.6121
-0.03	0.03	6.30	0.23	0.6122
-0.07	0.05	6.08	0.32	0.6121
0.02	0.05	6.26	0.12	0.6122
0.00	0.09	6.27	0.20	0.6122
0.02	0.07	4.06	0.24	0.6109
0.16	0.07	3.86	0.22	0.6107
				Mean = 0.6119 σ = 0.0006
THEORETICAL VALUES				
0.00		0.00		0.6084

The leakage rates of both gases into the ion source were adjusted until they measured 6 x 10^{-8}A. The ion source pressure of the sample and reference gases were then identical. The mass spectrometer was then operated under computer control, which automatically recorded twelve alternate measurements of the mass 29 and mass 40 ion currents and the 29/40 ratio for the reference and sample gases (Table 3.10). The mean of the reference ratio, the delta 29/40 and the $2\sigma_6$ value were determined.

3.5.2.2 Calibration Results

The method was calibrated with air equilibrated water. 10 l of distilled water were aerated for 2 hours, and then allowed to stand for a further 3 hours to exsolve excess air. Samples were collected (as described in section 3.5.1.2) and prepared for analysis.

The N_2/Ar ratio was generally enhanced above the theoretically expected ratio. Wide variation in the results occurred with σ = 13.73 for manually determined ratios (Table 3.11) and σ = 2.323 for the automated ratios (Table 3.12). Samples 1, 2 and 7 in Table 3.12 were below the theoretically expected value. Samples 4 and 6 were contaminated with atmospheric air and sample 3 and 5 had enhanced ratios. If excess air was incorporated then sample 3 would contain 2cm^3 and sample 5 would contain 3.9cm^3 (figure 3.10).

Fractionation was observed to occur. In both sets of air equilibrated water it was found that the volume of nitrogen was negatively correlated with the ^{15}N content (figure 3.11). The difference in magnitude of this effect between two sample sets could not be explained. The fractionation or isotopic trend may be the result of dilution of the slightly enriched (+0.07°/oo)[53] dissolved nitrogen by excess atmospheric air. It was not

TABLE 3.10 AN EXAMPLE OF OUTPUT FROM THE MASS SPECTROMETER CONTROL PROGRAM FOR 29/40 ANALYSIS A ZERO ENRICHMENT ANALYSIS

REF 29	38169
REF 40	101374
REF 29/40	0.377
SAM 40	104186
SAM 29	38975
SAM 29/40	0.374
REF 29	38209
REF 40	101424
REF 29/40	0.377
SAM 40	104221
SAM 29	39001
SAM 29/40	0.374
REF 29	38240
REF 40	101497
REF 29/40	0.377
SAM 40	104250
SAM 29	39009
SAM 29/40	0.374
REF 29	38253
REF 40	101517
REF 29/40	0.377
SAM 40	104283
SAM 29	39025
SAM 29/40	0.374
REF 29	38259
REF 40	101546
REF 29/40	0.377
SAM 40	104278
SAM 29	39047
SAM 29/40	0.374
REF 29	38280
REF 40	101546
REF 29/40	0.377
SAM 40	104267
SAM 29	39050
SAM 29/40	0.375
R BAR	0.377
DELTA 29/40	-6.58
2SIG6	0.23

TABLE 3.11 DETERMINATION OF $\delta^{15}N$ AND THE N_2/Ar RATIO ON AIR EQUILIBRATED WATER AT 27°C, BY MANUAL OPERATION OF THE MICROMASS 602E MASS SPECTROMETER

SAMPLE NO:	$\delta^{15}N$	$2\sigma_{10}$		RATIO 29/40	N_2/Ar
1.	1.74	0.02		0.3531	47.523
2.	1.57	0.01		0.3650	49.125
3.	1.10	0.02		0.4258	57.308
4.				0.5833	78.506
5.	0.42	0.02		0.5835	78.533
			Mean =	0.4621	62.194
			σ =	0.1141	13.733
Calculated value for air equilibrated water at 27°C				0.2811	37.828

TABLE 3.12 DETERMINATION OF THE $\delta^{15}N$ AND THE N_2/Ar RATIO OF AIR EQUILIBRATED WATER AT 21.6°C BY AUTOMATIC OPERATION OF THE 602E MASS SPECTROMETER

SAMPLE NO:	$\delta^{15}N$ o/oo	$2\sigma_{10}$	$\delta 29/40$	σ	RATIO 29/40	N_2/Ar
1.	21.58	0.02	-560.74	0.42	0.2672	35.968
2.	18.31	0.01	-542.23	0.94	0.2785	37.484
3.	12.15	0.05	-507.14	0.75	0.2997	40.335
4.	2.87	0.19	- 25.68	0.24	0.5928	79.781
5.	11.58	0.33	-482.20	3.68	0.3150	42.399
6.	1.46	0.03	-218.79	0.49	0.4753	63.969
7.	4.73	0.02	-543.25	0.59	0.2779	37.401
Calculated value of air equilibrated water at 21.6°C					0.2720	37.548
					Mean =	38.7174
					σ =	2.323
					Sample =	5

Note: Sample 4 - contaminated with atmospheric air
Sample 6 - contaminated with atmospheric air
} excluded from calculation of mean

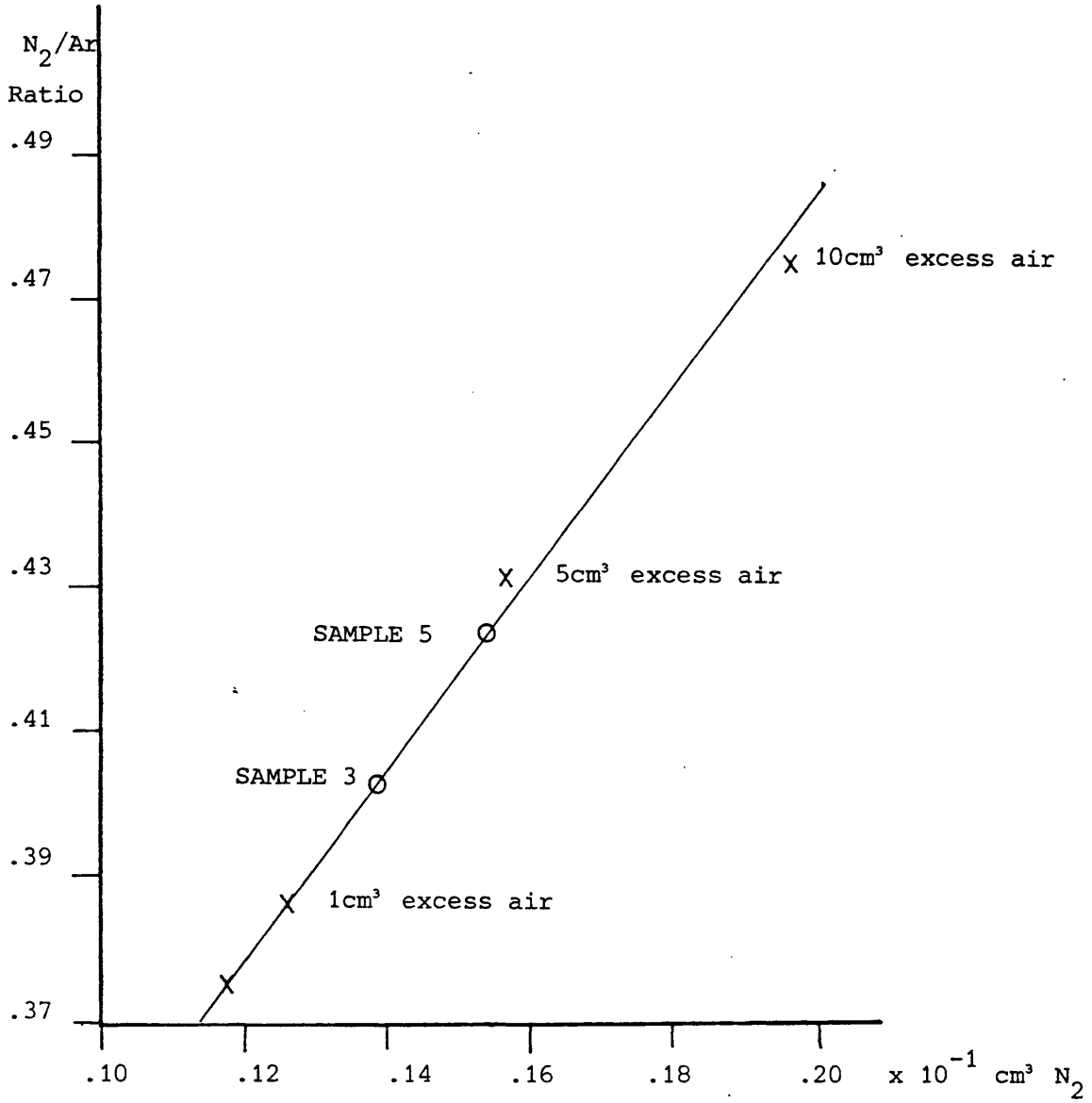


FIGURE 3.10 EXCESS AIR DISSOLVED IN AIR EQUILIBRATED DISTILLED WATER AT 21.6°C

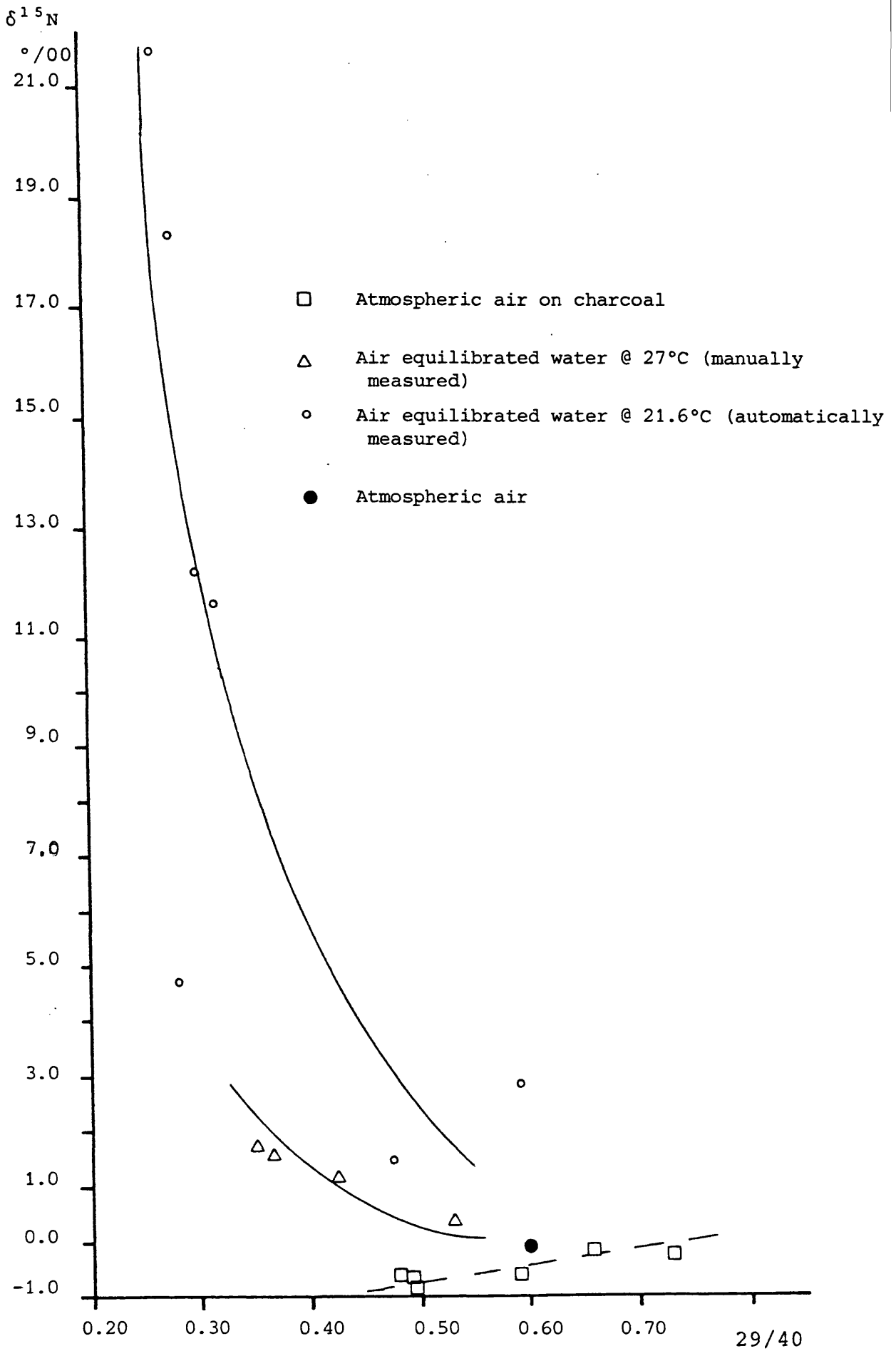


FIGURE 3.11 FRACTIONATION OF $^{15}N/^{14}N$ IN DISSOLVED NITROGEN

an effect of the experimental method since atmospheric air was directly absorbed on charcoal a positive relationship was observed between $\delta^{15}N$ content and the 29/40 ratio (figure 3.11). In this case the $\delta^{15}N$ value was negative (Table 3.13) and the ^{15}N atom appeared to be preferentially absorbed, agreeing with the previous observations (Table 3.1). The magnitude of this experimental isotopic effect was small in comparison to fractionation caused by the nitrogen water interaction. Every sample was absorbed on charcoal and since each was similarly affected no correction was made. Fractionation as a function of solution could not account for the high positive $\delta^{15}N$ values (Table 3.12). These samples were probably contaminated with oxides of nitrogen and carbon formed during the preparation process.

3.5.2.3 Precision and Accuracy

The automated method to determine the N_2/Ar ratio using the 602E mass spectrometer measured the dissolved N_2/Ar ratio of a standard water sample to within ±4.9 ratio units with σ=2.32. Thus field samples could be measured to this precision, although the effect of denitrification within the soil zone which alters the N_2/Ar by only a few percent could be masked. The error would account for approximately 13% of observed ratios varying between 36 and 40 units. However, where denitrification occurs within the aquifer the N_2/Ar ratio may double to approximately 80 units. A semi-quantitative interpretation of the observed N_2/Ar ratios may be made, for here the error term would only account for 6%.

During the infiltration process excess air may be entrained, and especially in aquifers where turbulent flow occurs. Under such conditions the N_2 released by denitrification would be masked by the N_2 in excess air. Atmospheric air may also be incorporated in a sample during collection, and both these cases of contamination can be detected by interpretation of the $^{15}N/^{14}N$ ratio of the N_2. This contamination causes the poor reproducibility observed in field samples, and great care must be taken to explain it or reduce it.

TABLE 3.13 FRACTIONATION OF NITROGEN ISOTOPES OF ATMOSPHERIC N_2 ABSORBED ON CHARCOAL

SAMPLE	$\delta^{15}N°/oo$	σ	29/40
ATMOSPHERIC AIR	0.0		0.6084
CHARCOAL AIR	-0.63	0.01	0.4929
CHARCOAL AIR	-0.96	0.01	0.4910
CHARCOAL AIR	-0.66	0.01	0.4879
CHARCOAL AIR	-0.66	0.15	0.5973
CHARCOAL AIR	-0.16	0.01	0.6595
CHARCOAL AIR	-0.27	0.01	0.7312
			Mean = 0.5766
			σ = 0.1033

4. $^{15}N/^{14}N$ RATIO ANALYSIS

4.1 REVIEW OF PREVIOUS WORK

Determination of $^{15}N/^{14}N$ ratio is made on molecular nitrogen. Combined forms of the element are converted to nitrogen gas for analysis. Two methods of analysis are available; optical emission spectrometry can be used to analyse samples as small as 0.2µg to 10µg with a σ value of ±3%. A greater precision of ±0.5% is obtained with mass spectrometry where 30µg to 3mg of nitrogen is necessary dependent upon the instrumentation[195].

In this study the only combined form of nitrogen investigated was nitrate. Direct conversion of the NO_3^- to molecular nitrogen cannot be easily achieved without the production of nitrogen oxides which interfere with mass spectrometric isotope ratio analysis of nitrogen. Therefore, a two stage procedure was employed whereby NO_3^- is first reduced to an NH_4^+ form using the preferred Kjeldahl method, or the Dumas technique. The NH_4^+ species is then oxidized to N_2 gas. The Kjeldahl method has been used on seawater and on groundwater[5,128,132].

Contamination and isotope fractionation of N_2 gas must be eliminated or maintained at an acceptable value during the analytical process. Air, water vapour, alcohol[207] and hydrogen[208] will significantly alter the $^{15}N/^{14}N$ ratio due to production of ionized species in the mass spectrometer source. The pressure of O_2 and CO_2 in the sample can result in the formation of CO (mass 28). Heated (700°C) copper turnings and CuO, followed by a liquid N_2 trap have been used to remove that contamination[31,73,82].

Isotopic fractionation during the first conversion stage, reduction of NO_3^- to NH_4^+ by Kjeldahl distillation, has been reported to result in ^{14}N

enrichment[73]. However, acceptance variations of <±0.4°/oo for yields in excess of 72% have been observed[68]. In the second stage where the resulting NH_4^+ is oxidized, NaOBr is recommended[209] as the oxidizing agent, but unless the solution has been recently and carefully prepared, chemical yields are not quantitative and isotopic fractionation may occur[210,211]. Quantitative yields of N_2 are readily obtained using a rapid procedure with LiOBr as the oxidizing agent[212].

The natural abundance of ^{15}N in atmospheric nitrogen is constant within analytical precision, and is used internationally as the reference standard for $^{15}N/^{14}N$ determination.

A comparison may be made of the precision of measurement achieved for $^{15}N/^{14}N$ determination by other workers (Table 4.1). There is no agreed method of presenting the error terms, so a qualitative appraisal shows that the overall precision lies between 0.3°/oo and 1.22°/oo. Thus the aim of this study was to equal or improve upon the best precision.

4.2 PREPARATION OF N_2 FOR $^{15}N/^{14}N$ RATIO ANALYSIS FROM NITRATE

The preparation of N_2 from dissolved NO_3^- was carried out in three stages:

i) preconcentration of NO_3^- in the sample;

ii) the reduction of NO_3^- to NH_4^+;

iii) the oxidation of NH_4^+ to N_2.

4.2.1 PRECONCENTRATION OF NO_3^- IN THE SAMPLE

A minimum of 3mg of N_2 was required for analysis. Therefore, groundwater samples containing dissolved NO_3^- were concentrated from up to 25l

TABLE 4.1 A COMPARISON OF THE PRECISION OF $^{15}N/^{14}N$ RATIO DETERMINATION

REFERENCE	PRECISION
Cline and Kaplan (1975)[73]	±0.1°/oo @ 2σ Instrument Precision ±0.3°/oo @ 2σ Sample Precision
Letolle and Mariotti (1974)[132]	±0.3°/oo for $(NH_4)_2SO_4$ ±1.0°/oo for NO_3^-
Benson and Parker (1961b)[31]	±0.12°/oo for NO_3^-
Kreitler (1974)[128]	±1.04°/oo σ = 0.59 for NH_4Cl ±1.22°/oo σ = 1.06 for NO_3^-

to 250cm³ to obtain the equivalent concentration of NO_3^-. A rotary evaporator under reduced pressure at 50°C[73] was used.

4.2.2 THE REDUCTION OF NO_3^- TO NH_4^+

The concentrated solution was then quantitatively transferred to the Kjeldahl distillation apparatus (figure 4.1). The NO_3^- was reduced in NaOH with a catalyst, Devardas Alloy (50%Cu, 45%Al, 5%Zn) to NH_4^+, and recovered by steam distillation[209].

$$3NO_3^- + 8Al + 5OH^- + 2H_2O = 8AlO_2 + 3NH_3$$

3g of Devardas Alloy were added to the reaction vessel. Through the thistle funnel, up to 20cm³ of 20% NaOH was added to raise the pH to between 9.5 and 10. The flask was warmed to start the reaction and then allowed to stand for 1 hour. Ammonia was then recovered as $(NH_4)_2SO_4$. Distillation proceeded until 200cm³ of distillate filled the collecting flask in which 50cm³ standardized 0.1M H_2SO_4 was initially placed.

The excess H_2SO_4 was titrated to determine the chemical yield of the NO_3^- reduction. Before titration, the distillate was boiled for a few minutes to remove CO_2. The H_2SO_4 was titrated against 0.1M NaOH with bromothymol blue indicator. As soon as the end point was reached, the pH was reduced to pH3 to prevent escape of NH_3.

The distillate was then evaporated to dryness in a 20cm³ tube on a hotplate at 80°C, under infra-red lamps. $(NH_4)_2SO_4$ is non volatile, but must be evaporated at <pH3 in order to obtain quantitative yields[207]. The $(NH_4)_2SO_4$ could then be stored indefinitely in a dessicator until needed for analysis. The overall efficiency of preconcentration and

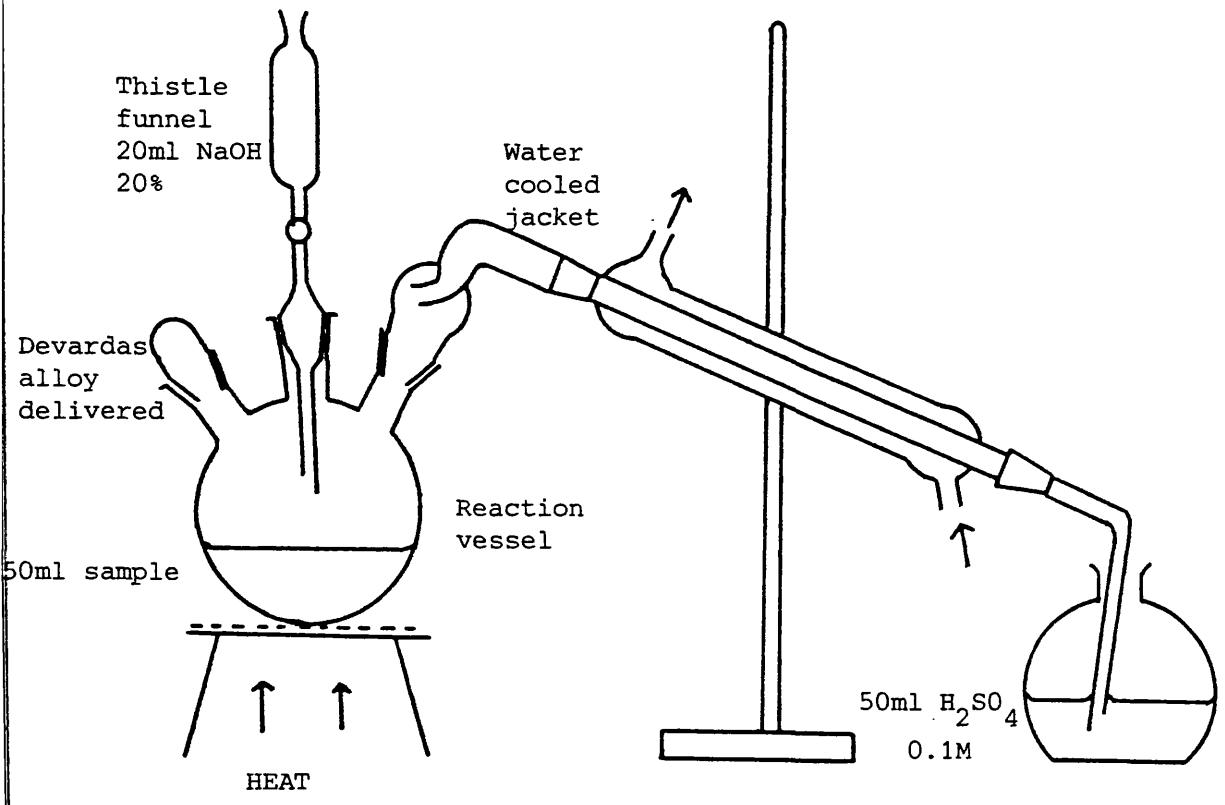


FIGURE 4.1 APPARATUS FOR THE REDUCTION OF NO_3^- TO NH_4^+

Kjeldahl reduction was greater than 90%.

4.2.3 THE OXIDATION OF NH_4^+ TO N_2

A rapid procedure for preparing gas samples for $^{15}N/^{14}N$ determination was developed. LiOBr was used as the oxidizing agent[212] where $1cm^3$ of the reagent oxidized 5mg of $NO_3.N$.

$$3LiOBr + (NH_4)_2SO_4 \rightarrow N_2 + 3LiBr + H_2SO_4 + 3H_2O$$

4.2.3.1 Apparatus

A glass vacuum preparation line (figure 4.2) was used to convert the prepared $(NH_4)_2SO_4$ to N_2 gas.

4.2.3.2 Reagent

LiOBr solution. $5cm^3$ A R Br_2 was added to $150cm^3$ of cold (0° to 5°C) 10% w/v solution of A R $LiOH.H_2O$. The mixture was stirred until the Br_2 dissolved.

4.2.3.3 Procedure

The LiOBr solution was placed in the reservoir (figure 4.2) and was outgassed with He to remove atmospheric N_2. A charcoal trap (figure 4.3), which had been previously baked at 400°C under vacuum to remove adsorbed gases, was connected as shown. The preparation line was then evacuated and a dry ice/alcohol bath was placed around the cold trap and another around the $20cm^3$ sample vial.

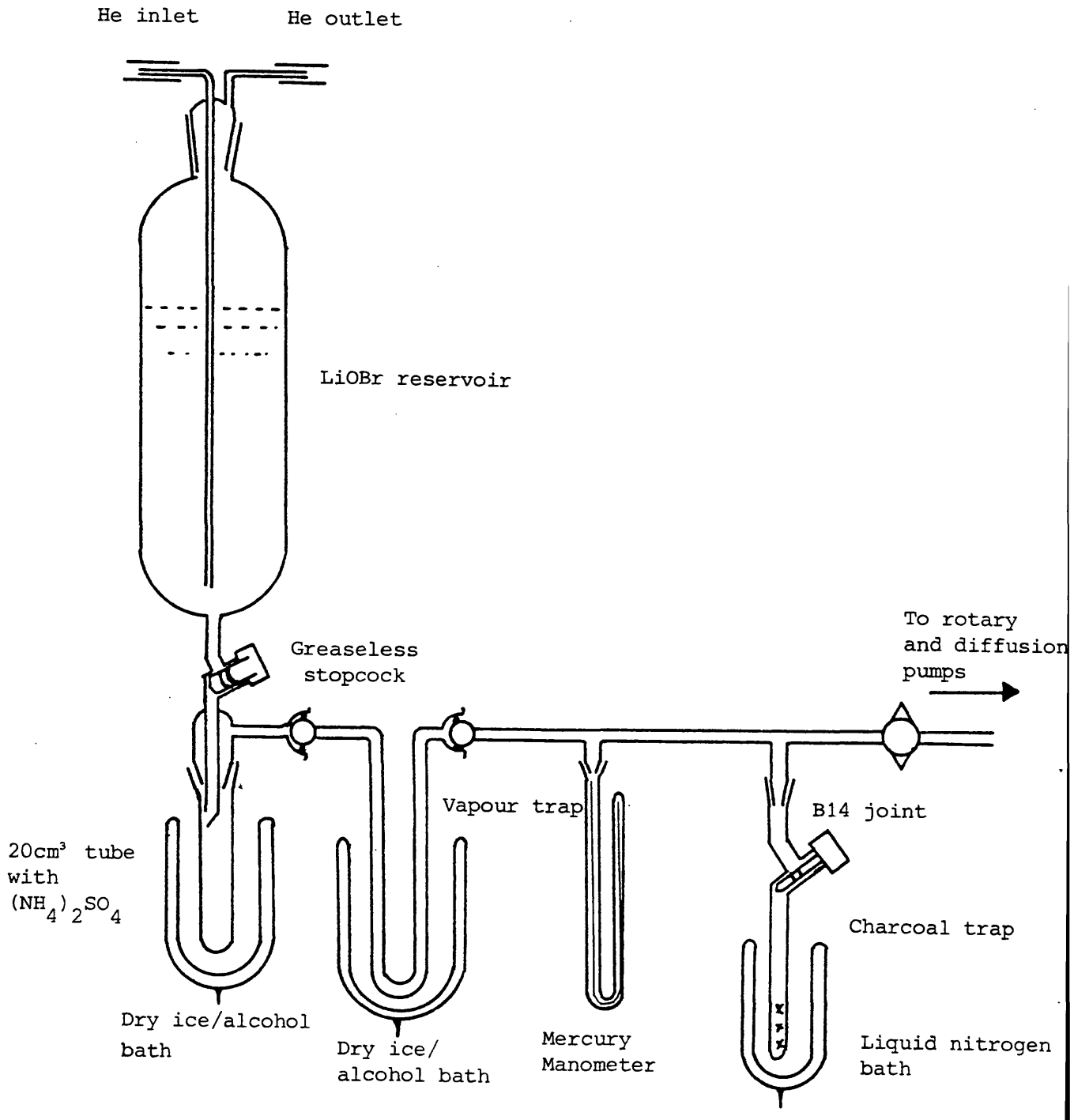


FIGURE 4.2 APPARATUS FOR THE OXIDATION OF $(NH_4)_2SO_4$ TO NITROGEN GAS

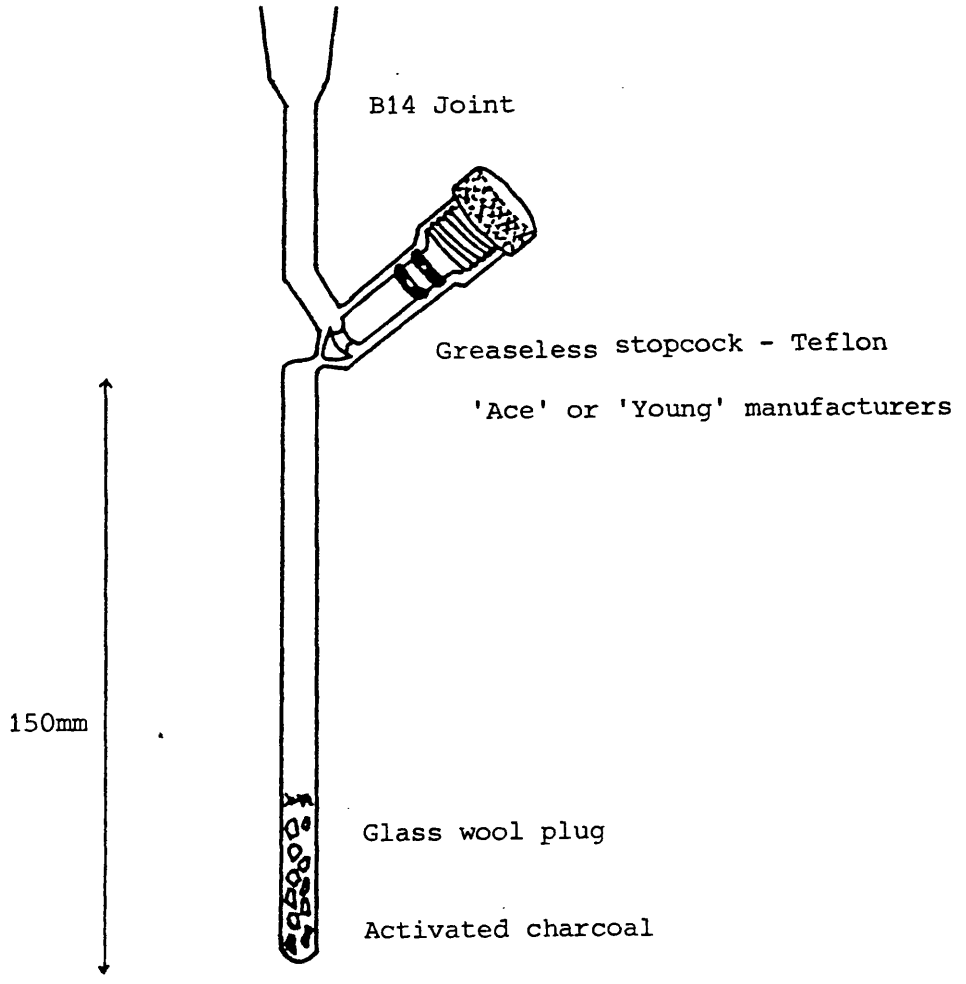


FIGURE 4.3 A CHARCOAL TRAP

Once a vacuum of 10^{-3} mb had been attained, the charcoal trap was opened and pumped; a liquid nitrogen trap was placed around it and the stopcock was again closed to isolate it.

The line was then shut off from the vacuum pumps, and the LiOBr solution was allowed gradually to flow into the 20cm³ tube. Addition of LiOBr was continued until the vigorous oxidation reaction ceased and the solution in the vial remained yellow. Nitrogen was then allowed to outgas from the solution into the line and the tap to the charcoal trap was then opened. The pressure in the line fell as the N_2 was absorbed by the charcoal and the stopcock was closed after 5 minutes. It was then removed for mass spectrometric analysis. The preparation line was made ready for the next sample by removing the cold trap for cleaning and replacing it together with another charcoal trap and sample vial.

The volume of N_2 required for mass spectrometer analysis was 50cm³ at 100mb. This required a minimum of 0.014g $(NH_4)_2SO_4$ and it was shown by the use of standard amounts of $(NH_4)_2SO_4$ that the conversion of N_2 was quantitative.

4.3 MASS SPECTROMETRY OF NITROGEN

4.3.1 THE PRINCIPLES OF MASS SPECTROMETRY

A mass spectrometer separates ions into a spectrum according to their mass or ratio of mass to charge (M/e). Separation is achieved by a combination of electrical and magnetic fields. The relative abundances of ions of different M/e ratios are determined by collection of the ions on one or two insulated electrodes and by measuring the currents produced.

A mass spectrometer designed for gas analysis essentially comprises five components (figure 4.4a):

i) an inlet system for introduction of the nitrogen gas;

ii) an ion source where the neutral molecules are bombarded with electrons, produced by a tungsten filament. The electron beam causes dissociation and ionization of complex molecules. Molecular nitrogen forms a number of charged species (Table 4.2). It is assumed that the nitrogen isotopes are in equilibrium. Therefore, the relative numbers of atoms of $^{14}N(p)$ and $^{15}N(q)$ in the gas give rise to molecular masses 28, 29 and 30 in the proportion:

$$p^2 : 2pq : q^2$$

and the isotopic ratio can be found by measurement of the ion currents corresponding to mass 28 ($^{14}N\ ^{14}N$) and mass 29 ($^{14}N\ ^{15}N$).

The ions are accelerated by negative potentials applied to the ion source, and pass to

iii) a magnetic field in which the charged molecules are separated with different paths according to their momentum. The ions travel in a circular path where the radius of curvature is dependent upon the mass and energy of the ions, heavy ions follow a path of greater radius than light ones according to:

$$M/e = 4.82 \times 10^{-5} H^2 r^2/v$$

M = mass of the ion in atomic mass units;

e = charge measured in terms of the number of electrons lost in ionization;

H = strength of the magnetic field in gauss;

r = radius of curvature of the ion path in centimetres;

v = accelerating potential in volts.

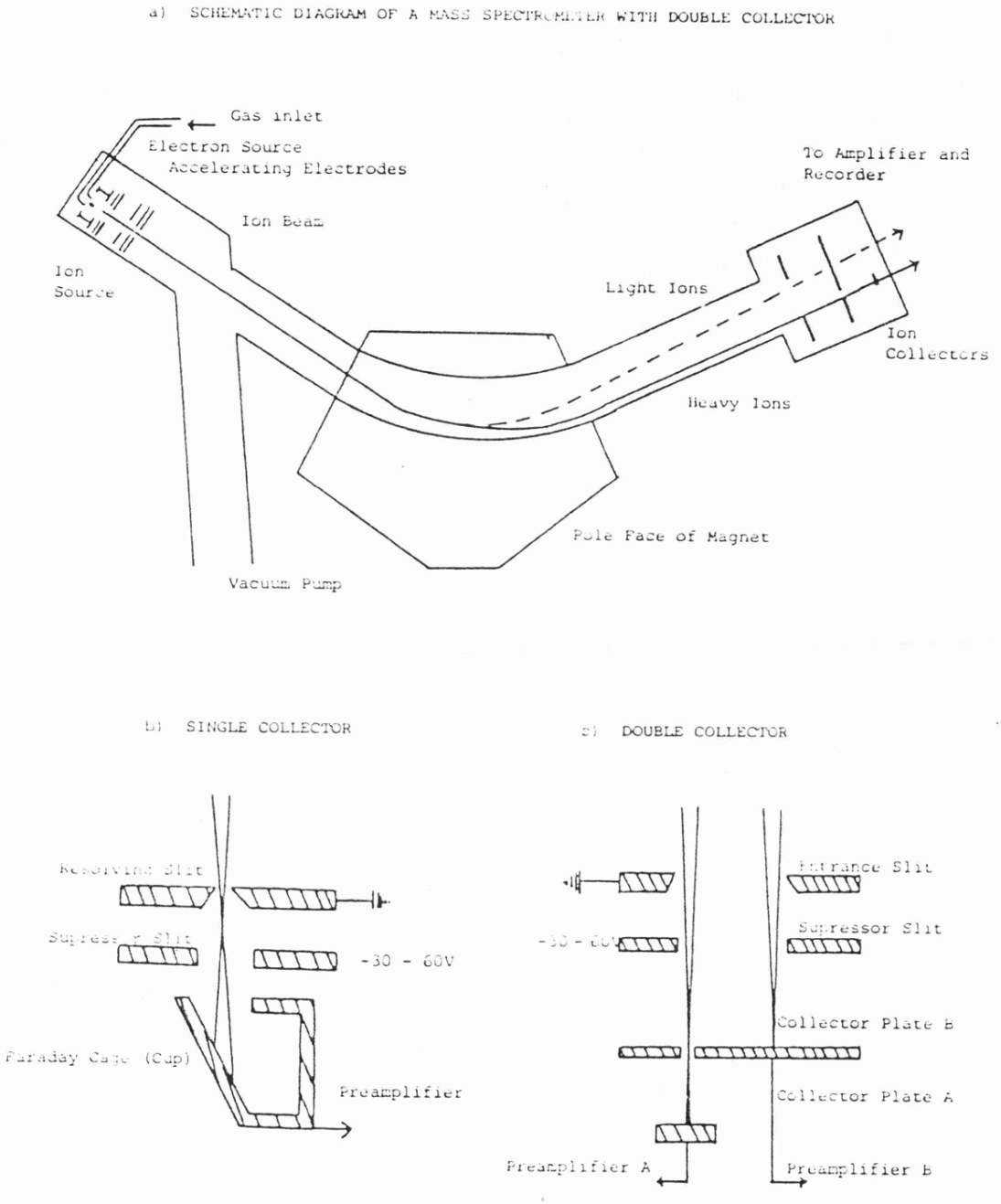


FIGURE 4.4 A DIAGRAMATIC CROSS SECTION OF A MASS SPECTROMETER,

AND SINGLE AND DOUBLE ION COLLECTORS

TABLE 4.2 IONS FORMED BY ELECTRON BOMBARDMENT OF MOLECULAR NITROGEN IN THE MASS SPECTROMETER

MASS NUMBER	ION
30	$(^{15}N^{15}N)^{+}$
29	$(^{14}N^{15}N)^{+}$
28	$(^{14}N^{14}N)^{+}$
15	$(^{15}N)^{+}$ and $(^{15}N^{15}N)^{2+}$
$14\frac{1}{2}$	$(^{14}N^{15}N)^{2+}$
14	$(^{14}N)^{+}$ and $(^{14}N^{14}N)^{2+}$

iv) the ions are focussed on a collector placed at the end of the flight tube where the molecules discharge, and the discharge currents are amplified. For stable isotope ratio analysis double collectors are employed and enable the simultaneous collection of the ions of the major and minor masses. If only a single collector (figure 4.4b) is used, then the ions of different masses are focussed to fall on the elctrode by altering H or V whilst the other is held constant. Double collectors have the advantages of greater precision, and fluctuations in the ion source are compensated for because all isotopes of interest are measured at the same time (figure 4.4c);

v) a recorder which registers the amplified discharge currents.

The accepted unit of isotopic ratio measurement is the delta value (δ), given in per mil (°/oo). The δ value is defined as:-

$$\delta \text{ in } °/oo = \frac{R \text{ sample} - R \text{ standard}}{R \text{ standard}} \times 1000$$

for nitrogen:-

$$\delta^{15}N°/oo = \frac{(^{15}N/^{14}N_{SAMPLE}) - (^{15}N/^{14}N_{STANDARD}) \times 1000}{(^{15}N/^{14}N_{STANDARD})}$$

The variation in natural abundance nitrogen isotope ratios is small, and will be significantly affected by instrumental error. Instrumental error may be random (eg ion beam fluctuations) or systematic (eg isotopic discrimination, non-linearity of amplifiers and defects in the optics). Systematic errors can be allowed for by calibration with a standard. Random instrumental errors are determined by analysing successive samples of a standard. No background corrections need be made and the observa-

tions are used directly to calculate instrumental variation. These errors are very small (<0.02‰)[11,213]. It is generally accepted that more precise ion current ratios are obtained with double collector systems than with a single ion beam collector, but satisfactory precision can be attained with the latter if sufficient replicate readings are taken.

4.3.2 $^{15}N/^{14}N$ RATIO ANALYSIS OF MOLECULAR NITROGEN

4.3.2.1 Apparatus

Mass spectrometer V G Micromass 602E Dual Collector and Double Inlet 90° sector of 6cm radius. 4 x 10^{10}ohms resistor for Major Amplifier 10^{11}ohms resistor for Minor Amplifier.

4.3.2.2 Procedure

A charcoal trap containing the sample was attached to the sample inlet of the mass spectrometer, and a reference gas to the reference gas inlet. A dried air sample was used as the reference.

The leakage rate of the gas sample and standard into the ion source of the mass spectrometer were adjusted until they measured approximately 6 x 10^{-8}A. The ion source pressure of both the sample and reference gas were then identical. The spectrometer was then operated under computer control which automatically recorded twelve alternate measurements of the $^{15}N/^{14}N$ ratio for the sample and reference gases. The mean $^{15}N/^{14}N$ ratio for the reference gas (air) and the sample, and the standard deviation for these were computed.

4.3.2.3 Calculation of the Results

The $\delta^{15}N$ values were calculated from the isotope ratios (R_S) of the sample, and compared with those for the reference gas (R_R). The data were collected by the program in the format shown in Table 4.3. The statistical calculations and corrections for instrument drift were made as outlined in Table 4.4. The results were considered unreliable if the $2\sigma_{10}$ value was >0.03.

4.3.2.4 Calibration Results

As a test of procedures, the $^{15}N/^{14}N$ ratio for atmospheric nitrogen recovered by adsorption on a charcoal trap as described above, was determined against atmospheric nitrogen standard. The results are presented in Table 4.5. The expected zero enrichment gave results with a mean positive enrichment of 0.08o/oo, ±0.08o/oo and a σ value of 0.115, where n=13. Where the sample size equals 8, then the mean $\delta^{15}N$ would be 0.03o/oo ±0.04o/oo. The latter was accepted as the instrument bias.

Air dissolved in distilled water gave a reproducibility with a mean of 6.98o/oo ±14.6o/oo, where n = 7. Slight contamination by water vapour or unexplained fractionation in the pretreatment of the sample may account for the variation. However, there are a few results with a mean $\delta^{15}N$ of 1.47°/oo ±0.27°/oo. These were considered to be uncontaminated and representative of the true value.

The $^{15}N/^{14}N$ ratio of a laboratory standard A R $(NH_4)_2SO_4$ was determined. The $\delta^{15}N$ was measured at -3.45°/oo ±0.65°/oo with a σ = 0.293 (Table 4.6). Therefore, the precision of the method of measurement, and of preparation of sample lies within the range achieved by previous workers.

TABLE 4.3 AN EXAMPLE OF OUTPUT FROM THE MASS SPECTROMETER CONTROL PROGRAM FOR A ZERO ENRICHMENT ANALYSIS

ANALYSIS OF 29/28

SAMPLE NO:	
SAM 28	40169
SAM 29/28	638761
REF 28	40136
REF 29/28	638748
SAM 28	40186
SAM 29/28	638695
REF 28	40295
REF 29/28	638747
SAM 28	40194
SAM 29/28	638705
REF 28	40319
REF 29/28	638727
SAM 28	40191
SAM 29/18	638722
REF 28	40308
REF 29/28	638697
SAM 28	40193
SAM 29/28	638673
REF 28	40289
REF 29/28	638696
SAM 28	40165
SAM 29/28	638639
REF 28	40278
REF 29/28	638691
R BAR	638718
DELTA 29/28	-0.04
2 SIG 10	0.02

TABLE 4.4 STATISTICAL CALCULATIONS OF δ AND $2\sigma_{10}$ USED IN THE CONTROL PROGRAM FOR THE MASS SPECTROMETER

SAMPLE	REFE-RENCE	DIFFERENCE S - R A	MEAN OF CONSECUTIVE READINGS IN COLUMN A B*	DEVIATION FROM X ($X_n - X$)	SQUARE DEVIATION FROM MEAN $(X_n - X)^2$
S_1		$S_1 - R_1 = A_1$	$\frac{A_1 + A_2}{2} = X_1$	$X_1 - \bar{X}$	$(X_1 - \bar{X})^2$
	R_1	$R_2 - R_1 = A_2$			
S_2		$S_2 - R_2 = A_3$	$\frac{A_2 + A_3}{2} = X_2$	$X_2 - \bar{X}$	$(X_2 - \bar{X})^2$
	R_2	$S_3 - R_2 = A_4$			
S_3		$S_3 - R_3 = A_5$	$\frac{A_3 + A_4}{2} = X_3$	$X_3 - \bar{X}$	$(X_3 - \bar{X})^2$
	R_3	$S_4 - R_3 = A_6$			
S_4		$S_4 - R_4 = A_7$	$\frac{A_4 + A_5}{2} = X_4$	$X_4 - \bar{X}$	$(X_4 - \bar{X})^2$
	R_4	$S_5 - R_4 = A_8$			
S_5		$S_5 - R_5 = A_9$	$\frac{A_5 + A_6}{2} = X_5$	$X_5 - \bar{X}$	$(X_5 - \bar{X})^2$
	R_5	$S_6 - R_5 = A_{10}$			
S_6		$S_6 - R_6 = A_{11}$	$\frac{A_6 + A_7}{2} = X_6$	$X_6 - \bar{X}$	$(X_6 - \bar{X})^2$
	R_6				
			$\frac{A_7 + A_8}{2} = X_7$	$X_7 - \bar{X}$	$(X_7 - \bar{X})^2$
			$\frac{A_8 + A_9}{2} = X_8$	$X_8 - \bar{X}$	$(X_8 - \bar{X})^2$
			$\frac{A_9 + A_{10}}{2} = X_9$	$X_9 - \bar{X}$	$(X_9 - \bar{X})^2$
			$\frac{A_{10} + A_{11}}{2} = X_{10}$	$X_{10} - \bar{X}$	$(X_{10} - \bar{X})^2$
	$\frac{\Sigma R_n}{6} = \bar{R}$		$\frac{\Sigma X_n}{10} = \bar{X}$		$\Sigma(x_n - \bar{X})^2$
	$\delta = \frac{\bar{X}}{\bar{R}} \times 10^3$ °/oo		$2\sigma_n = \frac{2\sqrt{\Sigma(X_n - X)^2}}{n - 1} \times 10^3$ R		

* This part of the calculation is included for the correction of linear drift in the ration reading during a run (due to changes in mass spectrometer characteristics or sample depletion).

TABLE 4.5 REPLICATE $^{15}N/^{14}N$ RATIO DETERMINATIONS ON DRIED ATMOSPHERIC N_2 AND DISSOLVED ATMOSPHERIC N_2 IN DISTILLED WATER

SAMPLE	$\delta^{15}N°/oo$	$2\sigma_{10}$	
DRIED AIR	-0.16	0.02	MEAN = 0.08o/oo ± 0.08o/oo where n = 13 σ = 0.115
	0.01*	0.01	
	-0.04*	0.01	
	-0.01*	0.02	
	0.14	0.02	
	-0.03	0.01	
	0.02*	0.01	
	0.13	0.01	
	0.06*	0.01	MEAN = 0.03o/oo ± 0.04o/oo where n = 8*
	-0.02*	0.03	
	0.03*	0.03	
	0.03*	0.03	
	-0.14	0.01	
AIR DISSOLVED INDISTILLED WATER	1.74*	0.02	MEAN = 1.47o/oo ± 0.2o/oo where n = 4*
	1.57*	0.01	
	1.10*	0.02	
	21.58	0.02	
	18.31	0.01	
	12.51†	0.05	
	2.87†	0.19	
	11.58†	0.33	
	1.46*	0.03	
	4.73	0.02	

† excluded from statistical treatment because $2\sigma_{10}$ value > 0.03

* values considered in calculation of mean

TABLE 4.6 REPLICATE $^{15}N/^{14}N$ RATIO DETERMINATION ON A R $(NH_4)_2SO_4$

$(NH_4)_2SO_4$ mg	$\delta^{15}N$	$2\sigma_{10}$
67	-4.10	0.03
67	-2.95	0.01
67	-3.03	0.02
46	-3.81	0.01
36	-3.45	0.02
36	-3.45	0.03
76	-3.64	0.01
57	-3.67	0.02
57	-3.40	0.01
57	-3.30	0.01
57	-3.22	0.02
56	-3.63	0.03
56	-3.32	0.02
MEAN $\delta^{15}N = -3.45°/oo \pm 0.65°/oo$, $\sigma = 0.293$ where n = 14		

5. TWO CASE STUDIES - THE NITROGEN HYDROGEOCHEMISTRY OF THE BERKSHIRE CHALK AND SOUTHERN LINCOLNSHIRE LIMESTONE

5.1 INTRODUCTION

High NO_3^- concentrations are found in recently recharged groundwaters below intensively cultivated agricultural land. In the UK, some of the most fertile soils are developed upon Mesozoic limestones which are also important aquifers. The hydrogeochemistry of the Berkshire Chalk (Cretaceous) and the Lincolnshire Limestone (Jurassic) were investigated to determine whether the nitrogen chemistry conformed to a simple redox controlled model[28], and using the techniques developed, to establish the rate and processes governing denitrification of polluting NO_3^-.

According to the redox chemistry NO_3^- is the dominant species in the unconfined and shallow confined aquifer. As the redox conditions of the aquifer environment change, the stability of NO_3^- decreases and NO_2^- is the dominant ion at the lower oxidation potentials. Molecular nitrogen is evolved with the onset of reducing conditions and NH_4^+ is the most reduced form occurring in the deep aquifer.

Both aquifers have high porosity and transmissivity values with movement of groundwater predominantly through fissures. However, the mode of recharge differs in that the infiltration rates in the Chalk may vary from more than 5m/hr through some fissures, to less than 1m/yr through intergranular seepage. The relative importance of the two mechanisms is not well understood. The Lincolnshire Limestone by contrast is karstic with a significant percentage of recharge entering the aquifer directly via the swallow holes,

and rates of movement of 30m/day in the aquifer were recorded[49]. A comparison was made between the effects of the different recharge processes on the advancement of contaminated groundwater and on the maintenance of a nitrogen hydrogeochemical equilibrium.

5.2 THE LINCOLNSHIRE LIMESTONE

5.2.1 A REVIEW OF THE HYDROGEOLOGY AND HYDROGEOCHEMISTRY

The field area was situated to the east of the southern part of the outcrop within a 25km radius of Bourne, South Lincolnshire. The Lincolnshire Limestone outcrops along a north-south line stretching 120km from the Humber to Kettering and is 14km wide (figure 5.1). At outcrop the land elevation is 120m OD. The Limestone dips at <1° eastwards and is concealed by a low lying district of reclaimed land known as 'the Fens'.

The Lincolnshire Limestone is 30m thick at outcrop and thins eastwards to <20m. The limestone exhibits considerable lithofacies changes both laterally and vertically, but two principal subdivisions are recognised. In the outcrop region, the lower part of the formation is a cemented oolitic limestone with locally sandy facies near the base. The upper half is a more massive freestone facies[214].

The limestone is confined beneath the clays, shales and marls with occasionally sands and limestones of the Great Oolite and Upper Estuarine Series, which vary in thickness from 4.5m to 14m. The Lincolnshire Limestone is underlain by a sequence of silts, clays and shales of the Lower Estuarine Series (Table 5.1).

Recharge to the Limestone is predominantly by direct precipitation. In

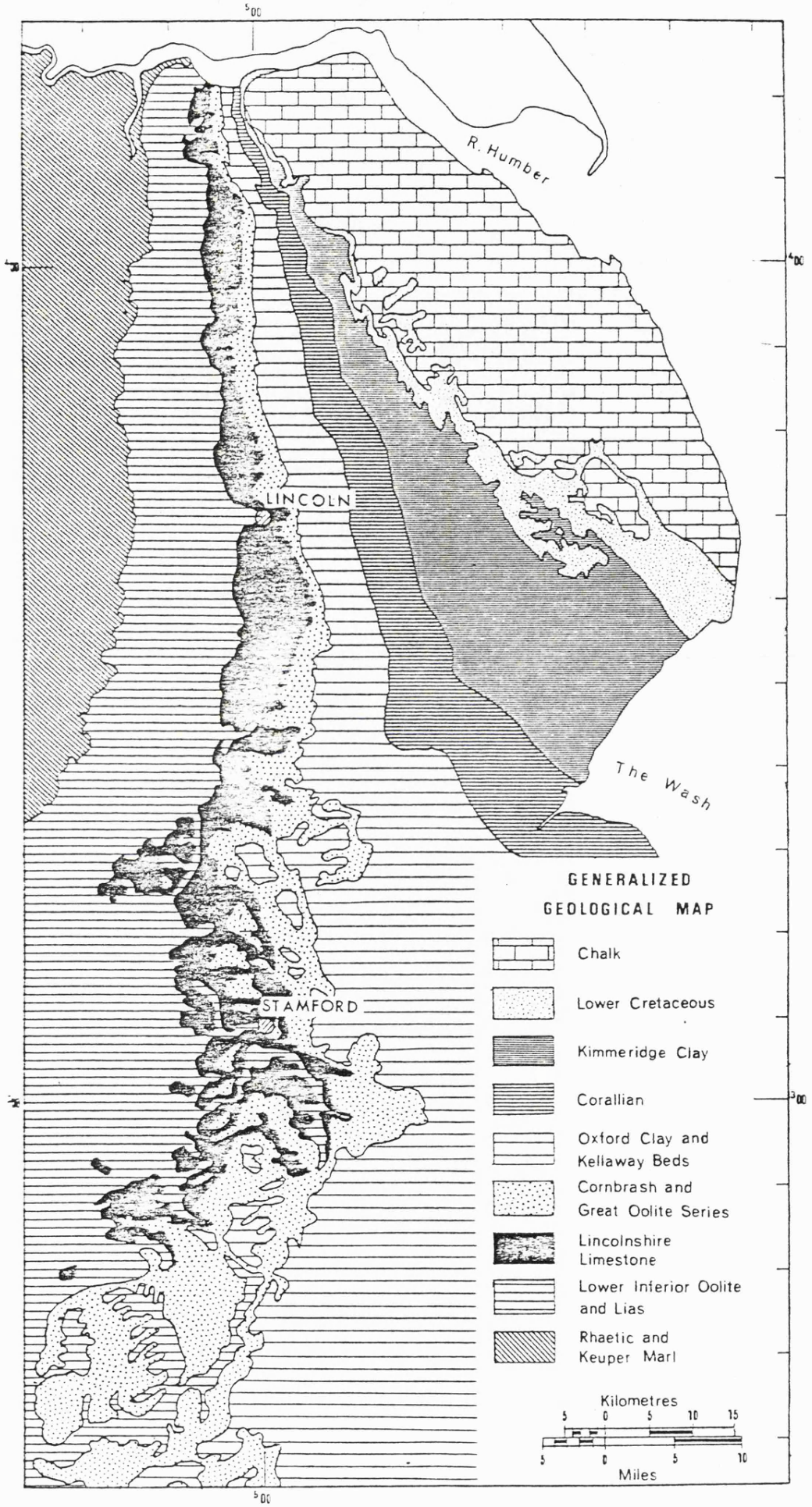


FIGURE 5.1 THE LOCATION OF THE LINCOLNSHIRE LIMESTONE[49]

TABLE 5.1 STRATIGRAPHY OF THE SOUTH LINCOLNSHIRE AREA[49]

			Lithology	Thickness feet	Thickness metres
Recent			Alluvium, Fenland gravels and sands, blown sand	variable	
Pleistocene			Boulder clay, glacial sand and gravel	variable	
Upper Jurassic		Kimmeridge Clay	Clay with cementstone bands	circa 600	circa 180
		Ampthill Clay	Clay		
		Oxford Clay	Clay with muddy limestones		
		Kellaways Beds	Calcareous sandstone passing down into clay	2 – 20	0·6 – 6
Middle Jurassic	Great Oolite Series	Cornbrash	Shelly limestone and ferruginous marl	1 – 10	0·3 – 3
		Great Oolite Clay	Clay and shale	6 – 40	2 – 12
		Great Oolite Limestone	Limestone with thin marl and clay beds	8 – 26	2·5 – 8
		Upper Estuarine Series	Sand, clay, shale and limestone	15 – 45	4·5 – 14
	Inferior Oolite Series	LINCOLNSHIRE LIMESTONE	Oolitic and argillaceous limestones with calcareous sandstones and cementstones	0 – 130	0 – 40
		Lower Estuarine Series	Sand, clay and shale	0 – 30	0 – 9
		Northampton Sand	Ferruginous sand and sandstone	0 – 36	0 – 11
Lower Jurassic	Lias	Upper Lias	Clay and shale with thin limestones	55 – 250	17 – 76
		Middle Lias	Ferruginous sandstone and clay	0 – 40	0 – 12
		Lower Lias	Clay and shale with thin limestones and ironstones	17 – 60	5 – 18

the outcrop region, the average annual rainfall is approximately 500mm/year. Recharge of surface run off, both via swallow holes and through the beds of 'losing' rivers is recognised as making a significant contribution[49,215,216].

Movement of groundwater is mostly through fissures. Transmissivities vary locally depending on the size and frequency of fissure development, and the position and distribution of abstraction sites. In South Linconshire, the limestone has a high transmissivity of approximately $1500m^2$/day, but is locally as high as 5000 to $10000m^2$/day. Well yields are typically $5000m^3$/day and range up to 25000 to $30000m^3$/day. A wide variation in the porosity of the limestone of the confined aquifer occurs, with an average of 13-18%. Permeabilities are very low, averaging 0.4 millidarcys giving hydraulic conductivities of 6×10^{-3} m /day. The configuration of the water table and piezometric surface reflect the total transmissibility, surface topography and discharge points of the aquifer[217,218]. Artesian discharge occurs for some 15km eastwards from outcrop.

Slow upward leakage from the Lincolnshire Limestone may occur through semi permeable overlying strata, and via buried channels of early Pleistocene age. Leakage may also occur through poorly maintained boreholes[219]. In the early 1970's recharge was below average, and during the 1976 drought the piezometric level dropped so that shallow confined boreholes were no longer artesian. Over abstraction has also depleted the aquifer, but with management it has recovered.

Leakage and fluctuating piezometric levels have modified the quality of the groundwater. The water chemistry undergoes a gradual transition. At outcrop Ca^{2+} and HCO_3^- are the dominant ions with variable amounts of SO_4^-. Downdip ion-exchange processes transform the water to the Na^+ and HCO^-_3

type. Sulphate decreases but H_2S is produced. The Cl^- concentration rises at 15-20km from outcrop to over 200mgl^{-1} and the higher salinities are attributed to a probable connate origin.

The oxidizing capacity of the groundwater decreases downdip and a sharp oxidation-reduction barrier occurs 12km from outcrop[47]. Up gradient of this barrier dissolved oxygen and nitrate occur, but downdip the oxygen declines to zero, and the NO_3^- decreases in concentration as the Fe^{3+} increases and dissolved sulphides appear.

The pH of the groundwater is relatively constant at pH7.2 for 16km from the outcrop[47]. Cation exchange reactions gradually remove Ca^{2+} from solution, and at 20km from outcrop the calcite solubility control is no longer effective and the pH increases. This rise is attributed to denitrification and SO_4^- reduction[19].

The hydrogeochemistry has remained relatively constant over a decade[221]. The carbonate equilibrium, oxygen reduction, ion-exchange reactions, the position of the saline water boundary, and the balance of the redox reactions at depth have not changed. Groundwater over abstraction and the effects of the 1975-1976 drought[217] have caused recently recharged water, polluted by chemical fertilizers to move rapidly eastwards. This has led to increased concentrations of Ca^{2+}, SO_4^{2-}, Cl^- and NO_3^-. The Eh change in the aquifer is less marked than it was 10 years ago, and the presence of small concentrations of NO_3^- may account for this. The advance of the contaminated water is considered to be defined by the high SO_4^- levels, however, the NO_3^- remains at concentrations near to the detectable limit at almost the same distance from the outcrop as ten years previously.

This discrepancy between NO_3^- and SO_4^{2-} indirectly suggests that the aquifer has a significant capacity for nitrate reduction over the period.

The present sampling was designed to further resolve this uncertainty.

5.2.2 THE LINCOLNSHIRE LIMESTONE HYDROGEOCHEMICAL SURVEYS 1979-1981

Three hydrogeochemical surveys were carried out to map the nitrogen chemistry in relation to the physico-chemical aquifer environment. In 1979 an extensive reconnaissance survey established the dominant nitrogen species zone from outcrop to the deep confined aquifer and identified the area where denitrification occurred. In subsequent years, fieldwork was concentrated upon the shallow confined aquifers in an attempt to determine the rate and the capacity of the groundwater for nitrate reduction, and the areal distribution of high NO_3^- waters.

A total of 32 wells were monitored on the Lincolnshire Limestone (figure 5.2). The results of the surveys are presented upon two lines of section, which correspond to the path of groundwater flow[220,222]. In the north of the area the flow is in an ESE direction, through a part of the aquifer where the limestone is thicker than average. The southern section follows the easterly flow path controlled by the regional dip of the strata. By relating the spatial variation of the nitrogen hydrogeochemistry to the groundwater flow, temperal variation is incorporated enabling the dynamics of the system to be determined.

The Physico-Chemical Groundwater Environment

At each site, the physico-chemical parameters were measured to define the hydrogeochemical environment and to detect any progressive or seasonal variation. These results (Tables 5.2 - 5.5) are displayed in two diagrams (figures 5.3 - 5.4).

The pH and Eh controlling the nitrogen species stability changed with passage downdip along both sections. On the northern section the chemistry

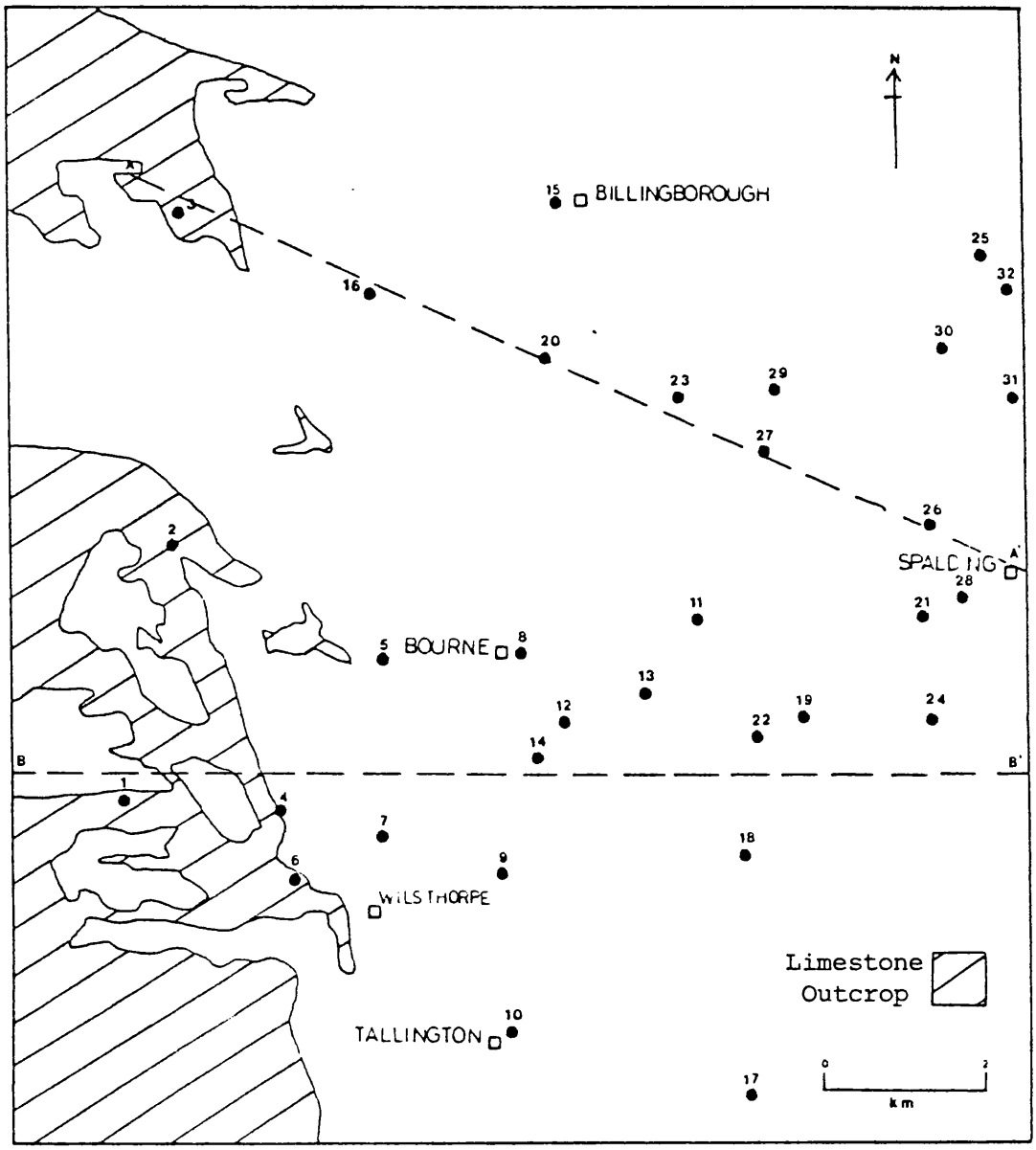


FIGURE 5.2 THE OUTCROP OF THE LINCOLNSHIRE LIMESTONE AND THE LOCATION OF SAMPLE BOREHOLES IN SOUTH LINCOLNSHIRE

TABLE 5.2 pH OF LINCOLNSHIRE LIMESTONE GROUNDWATERS 1979-1981

No.	Name	Km from Outcrop	pH 1979	pH 1980	pH 1981
1.	Clipsham	0.00	7.15	6.80	-
2.	Swayfield	0.00	7.05	7.35	-
3.	Ropsley	0.00	7.35	-	-
4.	Careby	0.00	-	7.05	7.35
5.	Pasture Hill	0.00	-	6.25	-
6.	Carlby	0.00	-	-	6.85
7.	Bowthorpe	2.53	-	-	7.15
8.	Bourne	5.15	7.15	6.85	6.85
9.	Braceborough	5.63	7.15	-	7.15
10.	Tallington	6.34	7.05	-	-
11.	Twenty	7.05	-	6.90	7.15
12.	Northorpe	7.60	-	6.05	6.90
13.	Black House Fm	8.00	-	6.45	-
14.	Thurlby	8.20	-	6.35	-
15.	Billingborough	9.65	7.10	-	-
16.	Lenton	12.45	7.55	-	-
17.	Sixscore Farm	13.13	8.25	-	-
18.	Peakirk	12.23	7.20	-	-
19.	Pepper Hill	16.41	7.85	-	7.65
20.	Dowsby Hall Farm	16.73	7.25	-	-
21.	Horseshoe Bridge	17.86	7.90	-	-
22.	Tongue End	18.02	7.80	-	-
23.	Rippingale	19.31	7.15	-	-
24.	Deeping RAC	20.17	8.20	-	9.05
25.	Quadring	20.60	7.65	-	-
26.	Newlands	22.92	8.40	-	-
27.	Jockey	22.20	7.20	-	-
28.	Spalding	22.20	8.35	-	-
29.	Vicarage Farm	22.37	7.45	-	-
30.	Cheal Bridge	27.51	7.85	-	-
31.	Surfleet	29.44	8.35	-	-
32.	Gosberton	30.87	8.30	-	-

TABLE 5.3 Eh OF LINCOLNSHIRE LIMESTONE GROUNDWATER 1979-1981

No.	Name	Km from Outcrop	Eh, mv 1979	Eh, mv 1980
1.	Clipsham	0.00	-	-
2.	Swayfield	0.00	-	-
3.	Ropsley	0.00	-	-
4.	Careby	0.00	-	-
5.	Pasture Hill	0.00	-	-
6.	Carlby	0.00	-	-
7.	Bowthorpe	2.53	-	-
8.	Bourne	5.15	+341	+ 46
9.	Braceborough	5.63	+306	-
10.	Tallington	6.34	+213	-
11.	Twenty	7.05	-	+117
12.	Northorpe	7.60	-	- 45
13.	Black House Fm	8.00	-	-149
14.	Thurlby	8.20	-	-
15.	Billingborough	9.65	[+721]	-
16.	Lenton	12.23	+ 74	-
17.	Peakirk	12.45	+140	-
18.	Sixscore Farm	13.13	+221	-
19.	Pepper Hill	16.41	+155	-
20.	Dowsby Hall Farm	16.73	+341	-
21.	Horseshoe Bridge	17.86	+149	-
22.	Tongue End	18.02	+ 90	-
23.	Rippingale	19.31	+ 17	-
24.	Deeping RAC	20.27	- 51	-
25.	Quadring	20.60	-188	-
26.	Newlands	20.92	+391	-
27.	Jockey	22.20	+245	-
28.	Spalding	22.20	- 6	-
29.	Vicarage Farm	22.37	+270	-
30.	Cheal Bridge	27.51	+ 53	-
31.	Surfleet	29.44	+ 41	-
32.	Gosberton	30.87	- 91	-

TABLE 5.4 DISSOLVED OXYGEN OF LINCOLNSHIRE LIMESTONE GROUNDWATERS 1979-1981

No.	Name	Km from Outcrop	Dissolved O_2 mgl^{-1} 1979	Dissolved O_2 mgl^{-1} 1980	Dissolved O_2 mgl^{-1} 1981
1.	Clipsham	0.00	10.30	-	-
2.	Swayfield	0.00	-	-	-
3.	Ropsley	0.00	11.60	-	-
4.	Careby	0.00	-	-	-
5.	Pasture Hill	0.00	-	-	-
6.	Carlby	0.00	-	-	-
7.	Bowthorpe	2.53	-	-	-
8.	Bourne	5.15	0.50	0.50	0.42
9.	Braceborough	5.63	0.40	-	0.30
10.	Tallington	6.34	0.30	-	-
11.	Twenty	7.05	-	0.40	0.54
12.	Northorpe	7.60	-	0.10	0.40
13.	Black House Fm	8.00	-	0.20	-
14.	Thurlby	8.20	-	0.20	-
15.	Billingborough	9.65	0.50	-	-
16.	Lenton	12.23	7.50	-	-
17.	Peakirk	12,45	<0.25	-	-
18.	Sixscore Farm	13.13	<0.25	-	-
19.	Pepper Hill	16.41	0.40	-	-
20.	Dowsby Hall Farm	16.73	0.65	-	0.40
21.	Horseshoe Bridge	17.86	<0.25	-	-
22.	Tongue End	18.02	0.65	-	-
23.	Rippingale	19.31	<0.25	-	-
24.	Deeping RAC	20.27	<0.25	-	0.32
25.	Quadring	20.60	<0.25	-	-
26.	Newlands	20.92	<0.25	-	-
27.	Jockey	22.20	0.30	-	-
28.	Spalding	22.20	<0.25	-	-
29.	Vicarage Farm	22.37	<0.25	-	-
30.	Cheal Bridge	27.51	<0.25	-	-
31.	Surfleet	29.44	0.30	-	-
32.	Gosberton	30.87	<0.25	-	-

TABLE 5.5 TEMPERTURE OF LINCOLNSHIRE LIMESTONE GROUNDWATERS 1979-1980

No.	Name	Km from Outcrop	Temp 0°C 1979	Temp 0°C 1980	Temp 0°C 1981
1.	Clipsham	0.00	-	9.0	-
2.	Swayfield	0.00	8.8	9.0	-
3.	Ropsley	0.00	-	-	-
4.	Careby	0.00	-	9.0	9.9
5.	Pasture Hill	0.00	-	10.2	-
6.	Carlby	0.00	-	-	10.6
7.	Bowthorpe	2.53	-	-	10.4
8.	Bourne	5.15	10.5	12.0	11.1
9.	Braceborough	5.63	9.5	-	11.0
10.	Tallington	6.34	11.1	-	-
11.	Twenty	7.05	-	12.0	13.2
12.	Northorpe	7.60	-	11.0	11.4
13.	Black House Fm	8.00	-	12.0	-
14.	Thurlby	8.20	-	10.7	-
15.	Billingborough	9.65	10.8	-	-
16.	Lenton	12.23	10.4	-	-
17.	Peakirk	12.45	11.4	-	-
18.	Sixscore Farm	13.13	11.4	-	-
19.	Pepper Hill	16.41	11.2	-	12.2
20.	Dowsby Hall Farm	16.73	10.9	-	-
21.	Horseshoe Bridge	17.86	12.6	-	-
22.	Tongue End	18.02	11.6	-	-
23.	Rippingale	19.31	10.9	-	-
24.	Deeping RAC	20.27	12.7	-	12.6
25.	Quadring	20.60	13.2	-	-
26.	Newlands	20.92	9.1	-	-
27.	Jockey	22.20	11.8	-	-
28.	Spalding	22.20	12.2	-	-
29.	Vicarage Farm	22.37	11.4	-	-
30.	Cheal Bridge	27.51	12.1	-	-
31.	Surfleet	29.44	13.2	-	-
32.	Gosberton	30.87	13.1	-	-

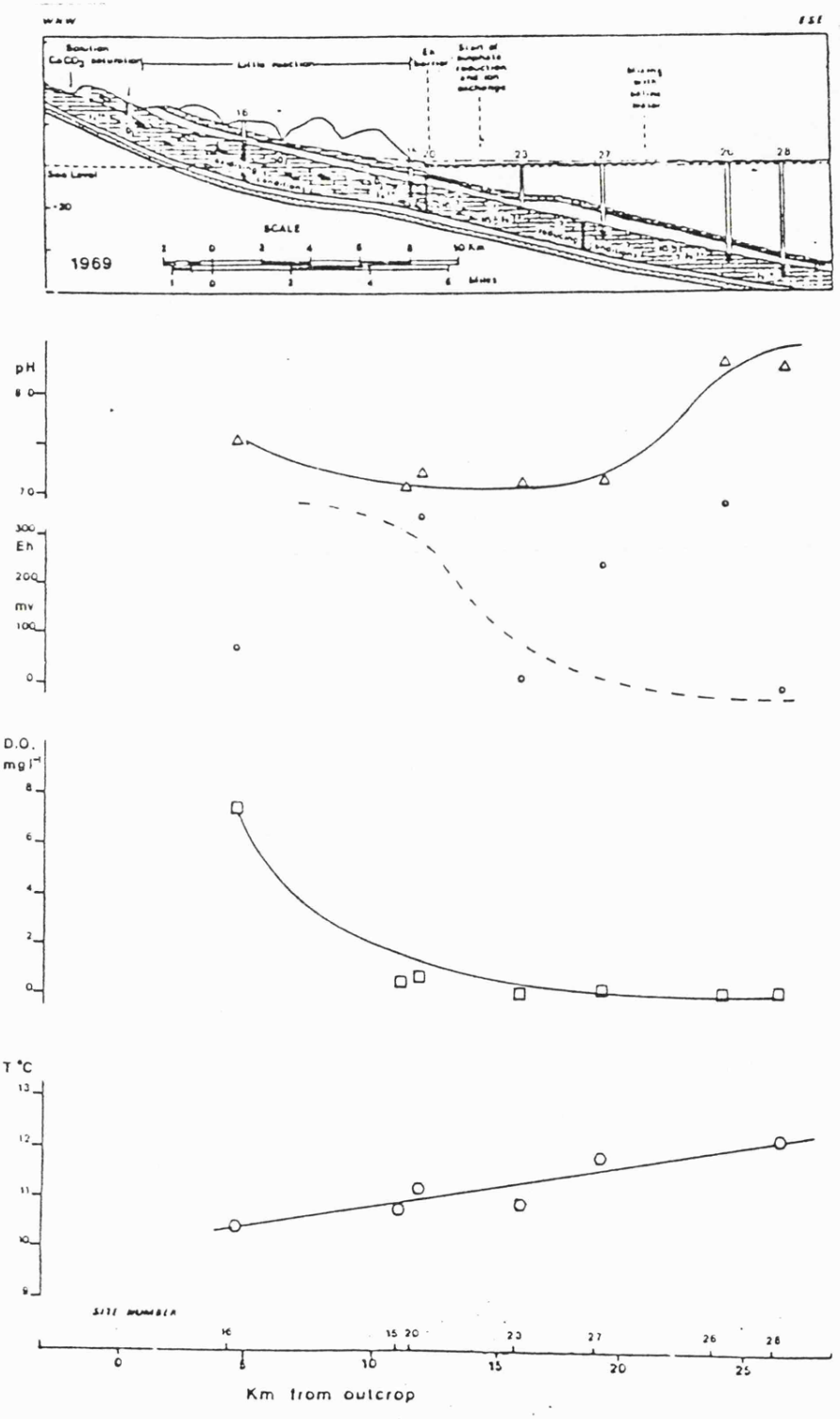


FIGURE 5.3 THE PHYSICO-CHEMICAL PARAMETERS OF THE LINCOLNSHIRE LIMESTONE GROUNDWATERS ALONG THE NORTHERN SECTION, 1979

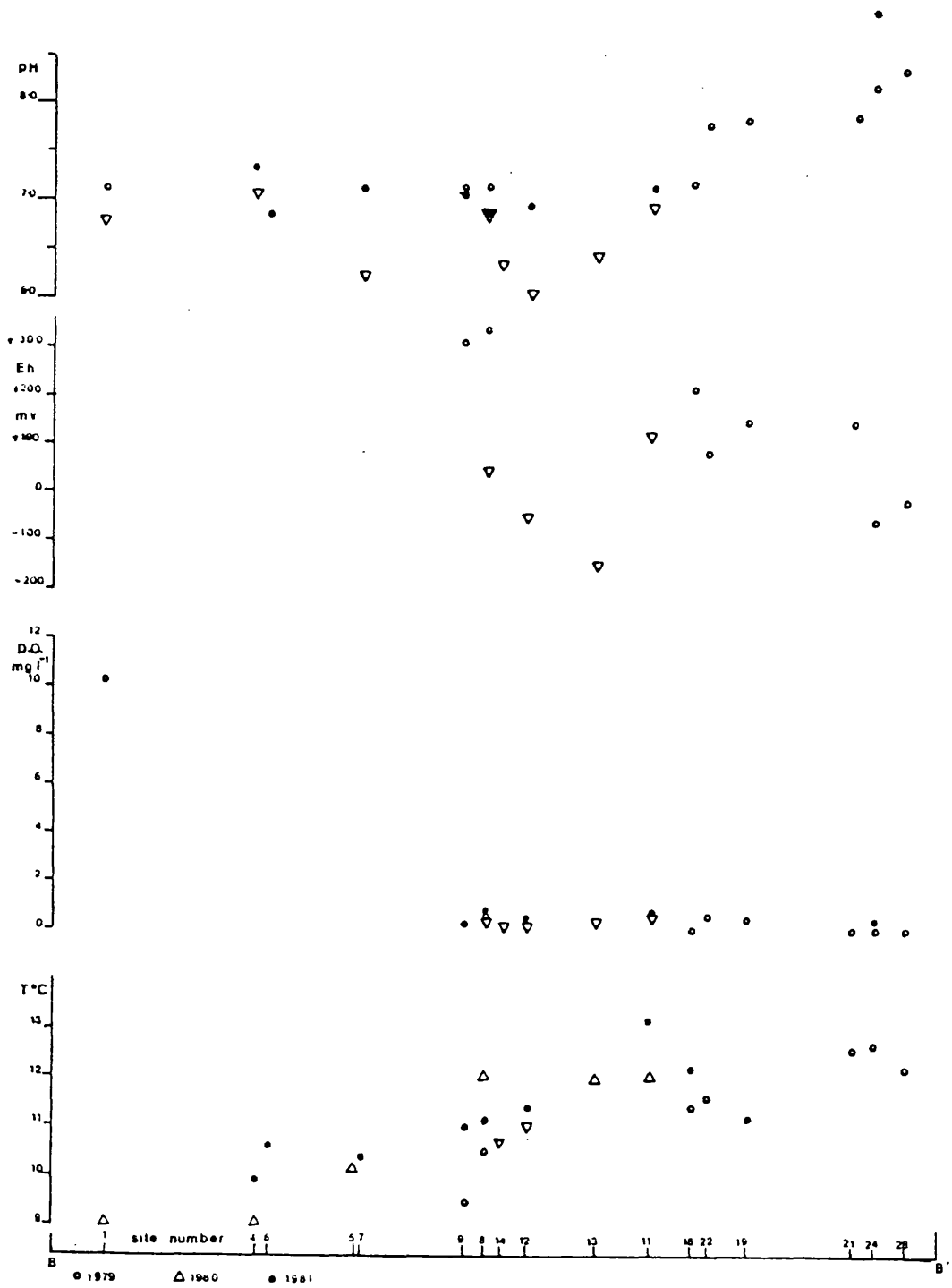


FIGURE 5.4 THE PHYSICO-CHEMICAL PARAMETERS OF THE LINCOLNSHIRE LIMESTONE ALONG THE SOUTHERN SECTION

was only monitored in 1979, but the range of the chemical characteristics, especially pH measurements,and their rise at about 20km from outcrop were closely allied to the three years of data for the southern section, and in agreement with earlier results[47]. The Eh results were rather variable, but when compared with the results of a contemporary survey[221] a marked decrease in the values could be identified at approximately 20km from outcrop in the northern section, and a little further east in the southern section. There was an apparent reduction in the Eh values between 1979 and 1980 in the south, but these can be explained by the use of different monitoring equipment.

Dissolved oxygen was reduced within a few km of the confined section of the aquifer. A gradual decrease was shown in the northern section; in the south no information existed for the unconfined and shallow confined area, but a similar trend was inferred. A marked annual variation occurred within the shallow confined aquifer where comparison was possible, reflecting annual or seasonal rapid recharge[224].

Dissolved Ionic Nitrogen Species and Chloride

The nitrogen species and chloride ion distributions are displayed in figure 5.5 for the northern section and in figure 5.6 for the southern section. In 1979 a complete survey of NO_3^-, NO_2^-, NH_4^+ and Cl^- was undertaken along both sections. In 1980 and 1981 only NO_3^- and Cl^- were monitored in the area of interest, which was confined to the southern section. The NO_3^- (Table 5.6) contents were high at outcrop (>60mgl^{-1}) and decreased rapidly within the aquifer following a similar trend to dissolved oxygen. Only traces of NO_3^- were present about 15km from outcrop. Nitrate (Table 5.6) showed a smooth decline in concentration along the northern section from Lenton (0.101mgl^{-1} NO_2^-) with background levels being reached at 15km distance. In the south a similar trend was indicated but the results showed greater variation since

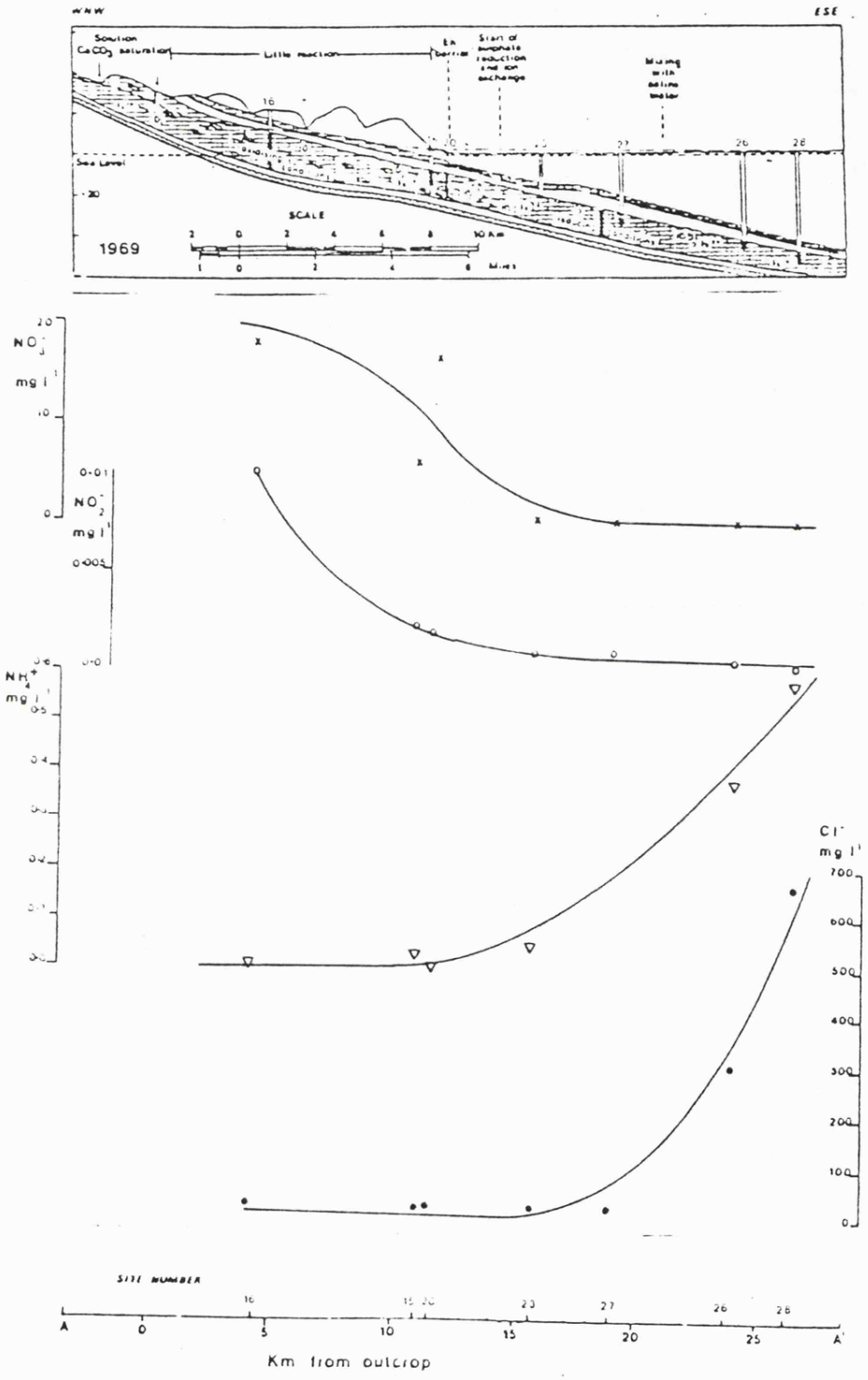


FIGURE 5.5 THE NITROGEN SPECIES AND CHLORIDE ION CONCENTRATION OF THE LINCOLNSHIRE LIMESTONE GROUNDWATERS ALONG THE NORTHERN SECTION, 1979

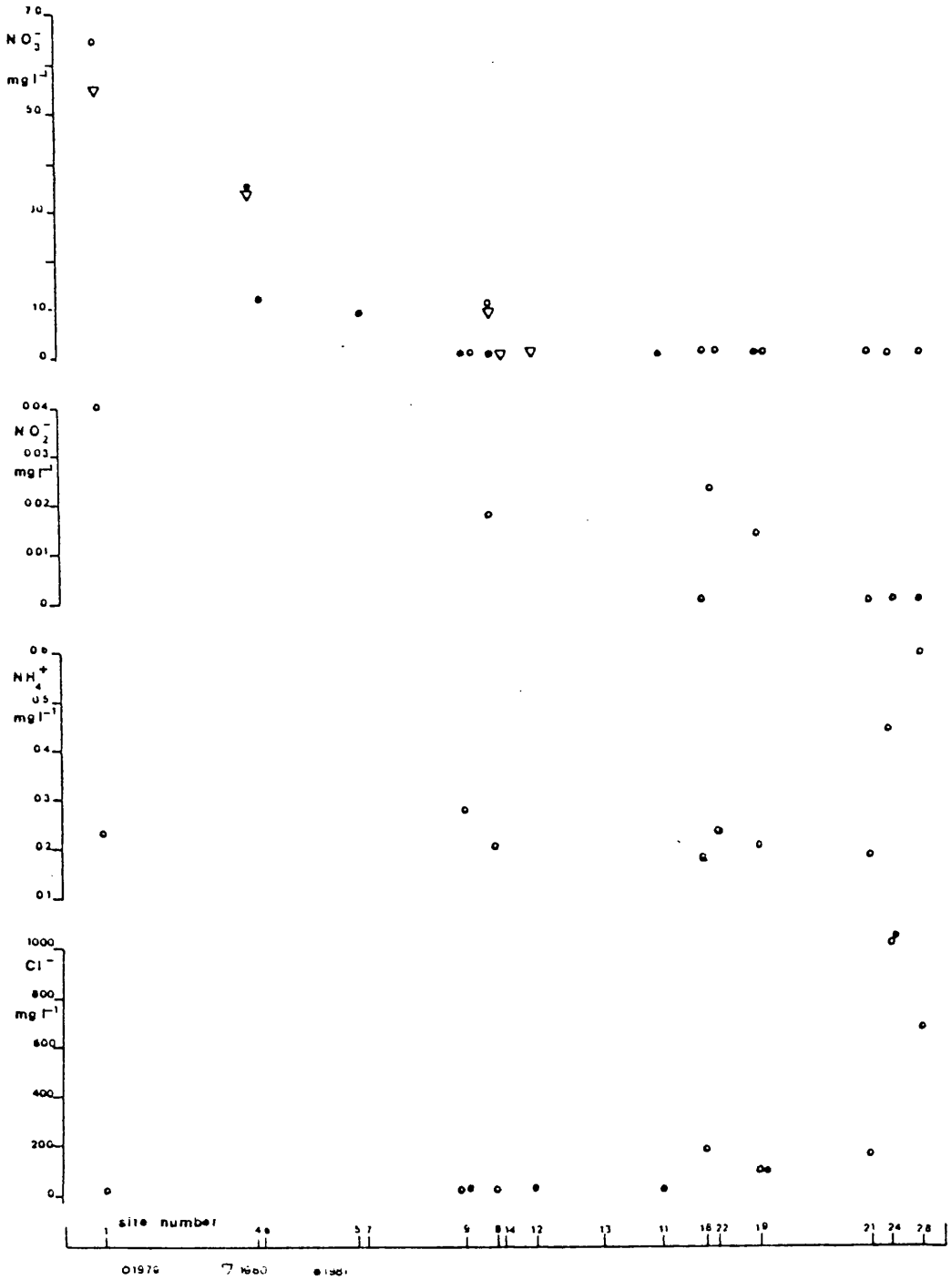


FIGURE 5.6 THE NITROGEN SPECIES AND CHLORIDE ION CONCENTRATION OF THE LINCOLNSHIRE LIMESTONE GROUNDWATERS ALONG THE SOUTHERN SECTION

TABLE 5.6 NITROGEN SPECIES OF LINCOLNSHIRE LIMESTONE GROUNDWATERS 1979-1981

No.	Name	NO_3^- mg^{-1} 1979*	NO_3^- mg^{-1} 1980†	NO_3^- mg^{-1} 1981†	NO_2^- mg^{-1} 1979	NH_4^+ mg^{-1} 1979
1.	Clipsham	65.43	55	-	0.041	0.023
2.	Swayfield	76.68	68	-	0.368	-
3.	Ropsley	22.75	-	-	0.005	0.026
4.	Careby	-	34	35	-	-
6.	Carlby	-	-	12	-	-
7.	Bowthorpe	-	-	9	-	-
8.	Bourne	10.48	10	<1	0.018	0.204
9.	Braceborough	0.05	-	<1	<0.005	0.283
10.	Tallington	0.11	-	-	<0.005	0.131
11.	Twenty	-	-	<1	-	-
12.	Northorpe	-	<1	<1	-	-
;4.	Thurlby	-	<1	-	-	-
15.	Billingborough	6.21	-	-	0.023	0.033
16.	Lenton	17.99	-	-	0.101	<0.020
17.	Peakirk	0.04	-	-	<0.005	-
18.	Sixscore Farm	0.07	-	-	<0.005	0.186
19.	Pepper Hill	0.04	-	<1	0.014	0.206
20.	Dowsby Hall Farm	16.64	-	-	0.018	<0.020
21.	Horseshoe Bridge	0.04	-	-	<0.005	0.183
22.	Tongue End	0.04	-	-	0.023	0.232
23.	Rippingale	0.02	-	-	0.009	0.053
24.	Deeping RAC	0.09	-	-	<0.005	0.443
25.	Quadring	0.87	-	-	0.023	0.425
26.	Newlands	0.09	-	-	<0.005	0.380
27.	Jockey	0.02	-	-	0.009	-
28.	Spalding	0.04	-	-	<0.005	0.559
29.	Vicarage Farm	0.02	-	-	<0.005	0.131
30.	Cheal Bridge	0.03	-	-	0.005	0.318
31.	Surfleet	0.04	-	-	0.023	0.047
32.	Gosberton	0.04	-	-	0.005	0.587

* = 167 † = 233

this line of section is not situated on just one flow line, but combines a number of easterly flowing groundwaters. At Swayfield (0.368mgl^{-1} NO_2^-) nitrite was most probably being produced in stagnant water in the borehole. Both NH_4^+ (Table 5.6) and Cl^- values (Table 5.7) increased with depth in the confined aquifer. In the north NH_4^+ was detected beyond 15km from outcrop with the Cl^- lagging slightly behind. Along the southern section both ions also increased beyond the 15km mark, but there was greater variation in the concentrations.

Nitrogen/Argon Ratio

The N_2/Ar ratio was determined at selected sites across the aquifer (Table 5.8) where the redox chemistry and nitrogen species distribution indicated the occurrence of nitrogen transformation processes. The replicate samples showed poor reproducibility (figure 5.7) and the causes for this have previously been discussed (Section 3.5.2.3). If 60mgl^{-1} NO_3^- were reduced in an air equilibrated groundwater, the N_2/Ar ratio would be increased to 64.134. Only samples with less than this value were possibly uncontaminated. Nevertheless, there is a trend which suggests that the N_2/Ar ratio increases as the redox barrier is approached and then declines.

Isotopic Composition of Dissolved Nitrogen

The $\delta^{15}N$ values of the dissolved N_2 were also very variable, and ranged between +3.56°/oo and -3.17°/oo (Table 5.8), the heavier value being typical of the soil zone. Fractionation of the nitrogen isotopes was demonstrated (figure 5.8), for in the shallow confined aquifer, the N_2 isotopic composition became lighter with increasing age, as indicated by the Cl^- content. This is evidence for the process of denitrification since the bacterial reduction processes would favour the production of the lighter isotopes. The

TABLE 5.7 CHLORIDE ION CONCENTRATIONS OF LINCOLNSHIRE LIMESTONE GROUNDWATERS 1978 AND 1981

No.	Name	Km from Outcrop	Cl^- mgl^{-1} 1979	Cl^- mgl^{-1} 1981
1.	Clipsham	0.00	33.5	-
2.	Swayfield	0.00	36.5	-
3.	Ropsley	0.00	41.5	-
4.	Careby	0.00	-	-
5.	Pasture Hill	0.00	-	-
6.	Carlby	0.00	-	-
7.	Bowthorpe	2.53	-	-
8.	Bourne	5.15	31.0	-
9.	Braceborough	5.63	28.5	29.5
10.	Tallington	6.34	29.0	-
11.	Twenty	7.05	-	18.6
12.	Northorpe	7.60	-	29.3
13.	Black House Fm	8.00	-	-
14.	Thurlby	8.20	-	-
15.	Billingborough	9.65	30.0	-
16.	Lenton	12.23	34.0	-
17.	Peakirk	12.45	-	-
18.	Sixscore Farm	13.13	191.0	-
19.	Pepper Hill	16.41	114.0	104.0
20.	Dowsby Hall Farm	16.73	31.5	-
21.	Horseshore Bridge	17.86	178.0	-
22.	Tongue End	18.02	-	-
23.	Rippingale	19.31	25.0	-
24.	Deeping RAC	20.27	1100.0	1150.0
25.	Quadring	20.60	246.0	-
26.	Newlands	20.92	308.0	-
27.	Jockey	22.20	31.0	-
28.	Spalding	22.60	664.0	-
29.	Vicarage Farm	22.37	26.5	-
30.	Cheal Bridge	27.51	93.0	-
31.	Surfleet	29.44	246.0	-
32.	Gosberton	30.87	776.0	-

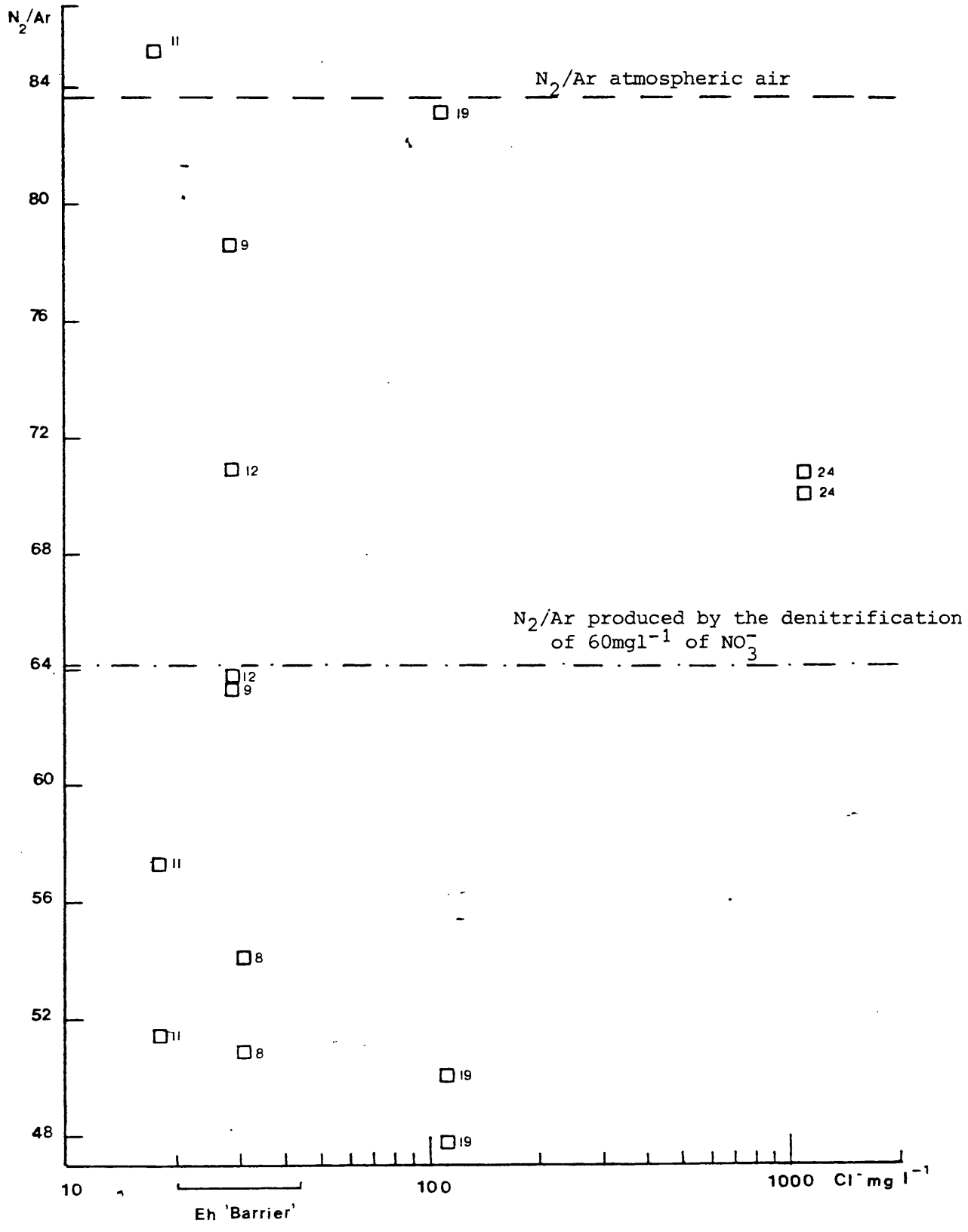


FIGURE 5.7 THE DISSOLVED N_2/Ar RATIO IN LINCOLNSHIRE LIMESTONE GROUNDWATERS ALONG THE SOUTHERN SECTION, 1981

TABLE 5.8 THE ISOTOPIC COMPOSITION OF DISSOLVED N_2 AND N_2/Ar RTIOS FOR LINCOLNSHIRE LIMESTONE GROUNDWATERS

Site No	NAME	δ^{15}No/oo	$2\sigma_{10}$	$^{29}/_{40}$	σ	N_2/Ar
8	Bourne	-0.73	0.03	0.4025	0.0004	54.145
		0.48	0.04	0.3782	0.0003	50.902
9	Braceborough	3.56	0.03	0.4631	63.328	
		0.21	0.04	0.5848	0.0021	78.708
10	Twenty	1.51	0.02	0.6331	0.0008	85.209
		1.08	0.01	0.3822	0.0007	51.440
		0.64	0.01	0.4259	0.0019	57.327
12	Northorpe	-0.01	0.03	0.5272	0.0038	70.956
		0.44	0.03	0.4747	0.0023	63.889
19	Pepper Hill	-0.90	0.04	0.3546	0.0060	47.725
		-3.22	0.03	0.3716	0.0060	50.013
		-2.16	0.02	0.6179	0.0006	83.163
24	Deeping RAC	0.73	0.01	0.5265	0.0007	70.861
		0.14	0.08	0.5207	0.0014	70.080

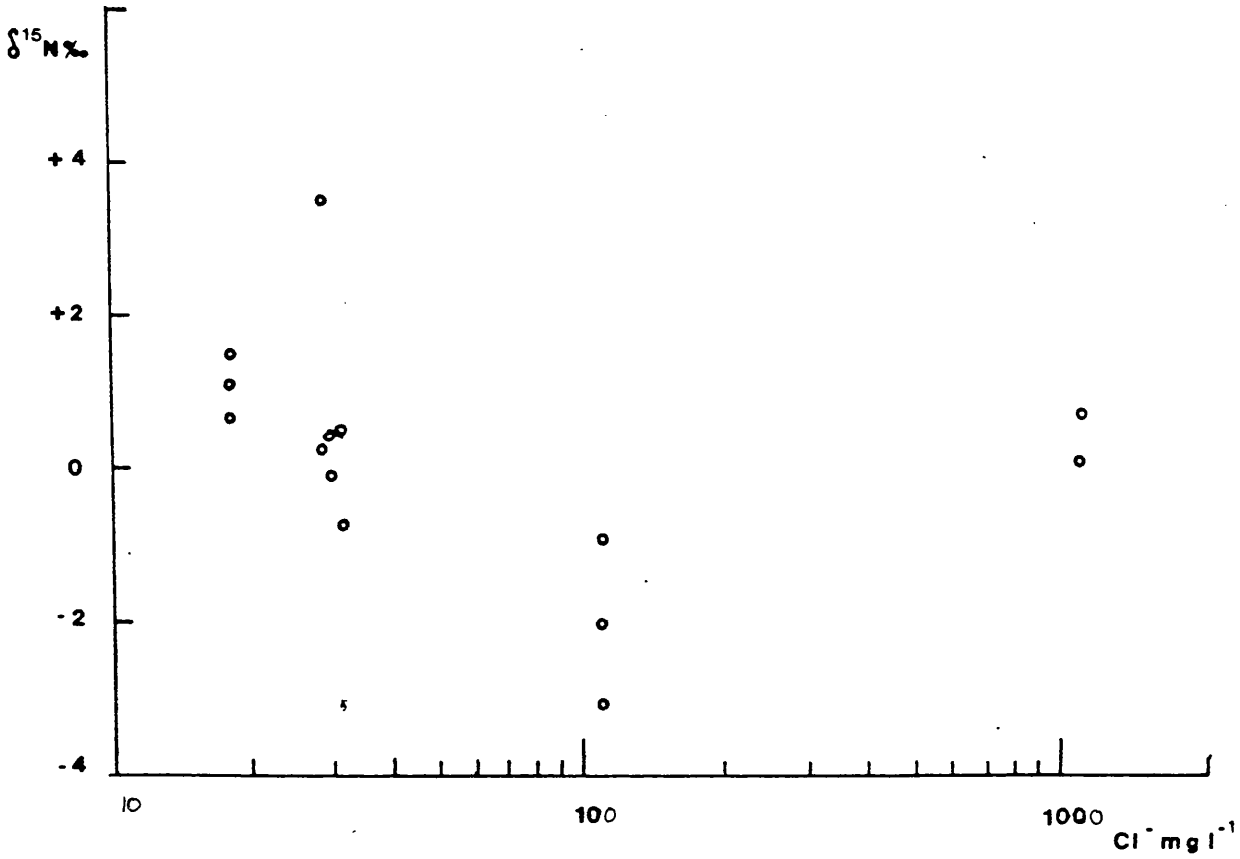


FIGURE 5.8 NITROGEN ISOTOPE COMPOSITION OF THE DISSOLVED NITROGEN IN THE LINCOLNSHIRE LIMESTONE GROUNDWATERS, 1981

$\delta^{15}N$ of the deep confined sample at Deeping RAC does not fit this decreasing trend and indicates another origin for the dissolved N_2.

The $\delta^{15}N$ values were also determined on the nitrogen derived from dissolved NO_3^- (Table 5.9). For sites on outcrop (Swayfield:- +2.77°/oo; Careby:- +7.69°/oo) the $\delta^{15}N$ values are characteristic of those for nitrate from the soil zone as described in Chapter 1 and reflects the overall inputs to, and processes within this horizon.

Microbiological Survey

In 1979 the microbiological population of Lincolnshire Limestone groundaters was investigated (Table 5.10). Sites deeper in the aquifer were shown to have a greater proportion of aneorobic bacteria (figure 5.9) than those nearer outcrop. At six of the sites anaerobic bacteria capable of denitrification were isolated. The three bacteria identified to species level Chromobacterium violateum, Psuedomonas indinium and Bacillus cereus v. mycoides were facultative aerobic denitrifiers, typical of the soil zone. Anaerobic denitrifying bacteria, the most probable active form of denitrifiers in the aquifer were only found at Lenton and Vicarage Farm. Correlation with the groundwater nitrite content, another indicator of denitrification suggested that at Lenton, the process of denitrification mediated by anaerobic bacteria was actively in progress.

5.2.3 DISCUSSION OF THE RESULTS OF THE LINCOLNSHIRE LIMESTONE HYDROGEOCHEMICAL SURVEYS

The hydrogeochemical sections of the Lincolnshire Limestone aquifer demonstrate that the redox chemistry primarily controls the distribution of the nitrogen species. The rapid decline in Eh values was coincident with

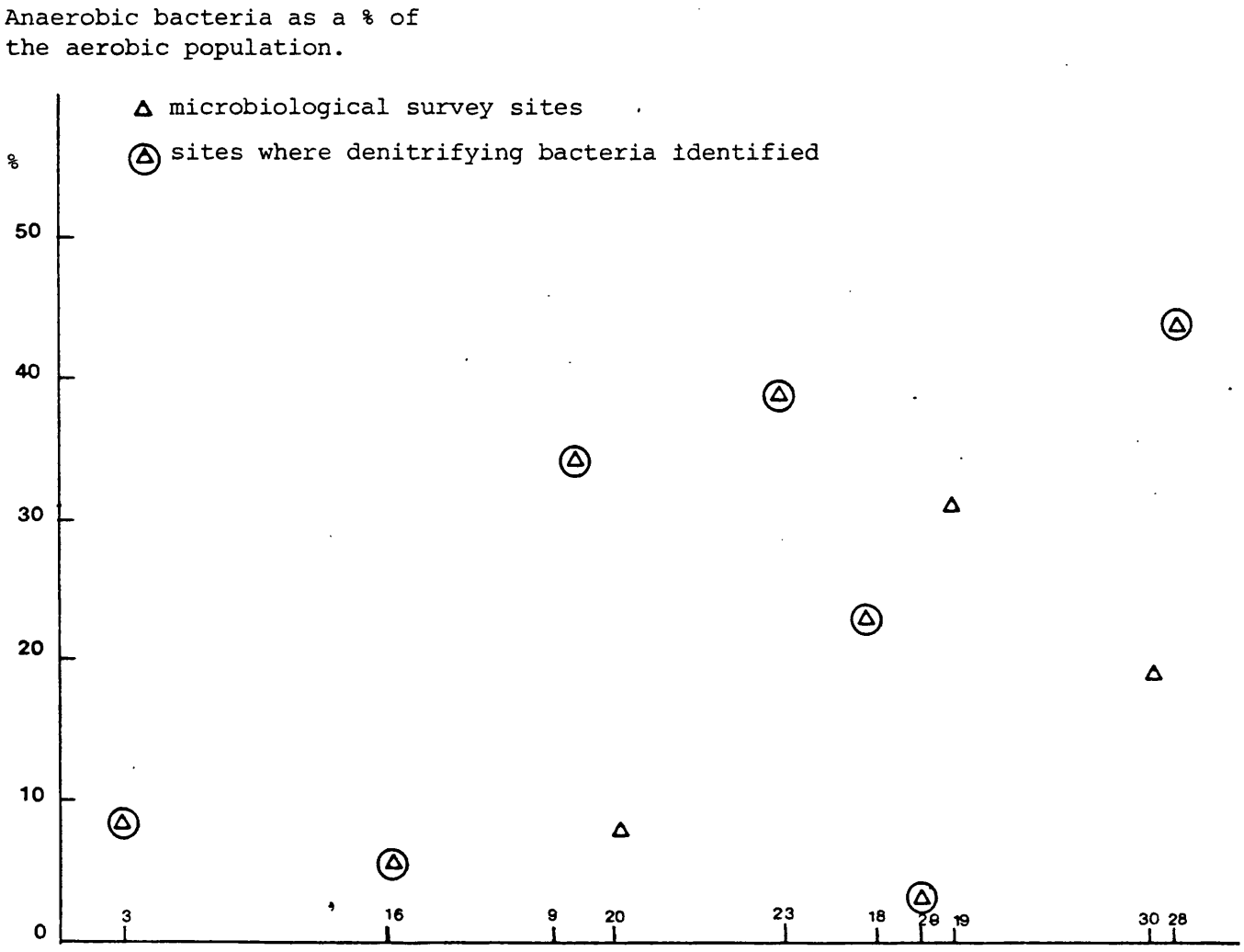
TABLE 5.9 THE ISOTOPIC COMPOSITION OF DISSOLVED NITRATE NITROGEN IN THE LINCOLNSHIRE LIMESTONE GROUNDWATERS

NO.	NAME	NO_3^- mgl^{-1}	δ^{15}No/oo	2σ
2	Swayfield	≈67	+2.91	0.02
			+2.96	0.02
			+2.66	0.02
			+2.55	0.03
			X = +2.77	
4	Careby	35	+7.61	0.03
			+7.77	0.02
			X = +7.69	

TABLE 5.10 BACTERIA OF THE LINCOLNSHIRE LIMESTONE GROUNDWATERS 1979

NO	SITE	TOTAL COUNT OF AEROBIC BACTERIA	TOTAL COUNT OF ANAEROBIC BACTERIA	ANAEROBES AS % OF AEROBIC POPULATION	DENITRIFYING BACTERIA SP IDENTIFIED AEROBIC	ANAEROBIC
3	Ropsley	2344	188	8	C.v.	-
9	Braceborough	1416	120	8	Z	-
16	Lenton	408	22	5	-	Y
18	Sixscore Farm	2092	480	23	C.v.	-
19	Pepper Hill	1372	420	31	-	-
20	Hall Farm	1476	120	8	-	-
23	Rippingale	1256	496	39	P.i.	-
28	Spalding	1176	520	44	X	-
29	Vicarage Farm	1184	32	3	B.c.m.	B.c.m.
30	Cheal Bridge	3556	684	19	-	-

	Survey Reference Numbers
C.v. = Chromobacterium violateum	318
P.i. = Pseudomonas indinium	324
B.c.m. = Bacillus cereus v. mycoides	325
X =	317
Y = unidentified denitrifying species	333
Z =	311



A combined North and South Section of the Lincolnshire Limestone

FIGURE 5.9 PROPORTION OF ANAEROBIC BACTERIA IN THE TOTAL BACTERIAL POPULATION OF GROUNDWATERS ACROSS THE LINCOLNSHIRE LIMESTONE, 1979

the decrease of NO_3^- and NO_2^- concentrations and marked the rise in NH_4^+ levels. For both sections however, this hydrogeochemical evolutionary model has been modified by abstraction.

Two distinct water types have been demonstrated in the Lincolnshire Limestone by the hydrogeochemistry and carbon isotopes[225]. Modern recharge water occurs in the west while saline water exceeding 25,000 years and unmixed with modern groundwater is found in the deep aquifer. Between the two water types a mixing zone has developed. This was exemplified by tritium measurements from around Bourne, Wilsthorpe and Tallington where heavy abstraction has brought older water from the east[226]. Along this southern section of the Limestone, groundwater high in NO_3^- is also being drawn from the west towards Bourne, beyond which point only trace amounts of NO_3^- are recorded. The sharp divide in physico-chemical conditions is therefore enhanced and maintained by pumping which tends to draw water from both east and west of the abstraction site.

A similar situation is found along the northern section where tritium has been used to show that recent water has penetrated the deeper aquifer along rapid flow fissures[49]. This recent water has been drawn by pumping at the Rippingale and Jockey stations, which effectively stops the passage of modern water further eastwards. Old saline water is drawn from storage in the west. These pumping stations also occur at the physico-chemical transition zone. The Eh 'barrier' which is reported[221] to be less marked than a decade ago may have been influenced by the abstraction. Therefore, in the Lincolnshire Limestone the hydrogeochemistry is now held in a steady state by abstraction, and movement of water to the east is controlled.

Nitrogen in Lincolnshire Limestone groundwaters has two possible sources. These are, first, modern recharge, which contributes dissolved nitrate.

The second and less significant source is from old saline water containing reduced nitrogen species ultimately derived from connate pore waters and the sediments. However, the NH_4^+ in the deep aquifer can be entirely accounted for by the accumulation of reduced nitrogen species from recharge.

All the groundwater derived from a meteoric source will have equilibrated with atmospheric nitrogen in the soil zone dissolved according to the equation:

$$[N_2] = S_T P_{N_2} \ (cm^3 \ STP \ cm^{-3} \ H_2O)$$

where S_T is the solubility of N_2 at 1 atmospheric pressure and the temperature of recharge T; and P_{N_2} is the partial pressure of N_2 in the atmosphere. At the present recharge temperature of 10°C, 1.47×10^{-2} cm^3/cm^3 is theoretically dissolved at atmospheric concentrations, but in the soil zone the partial pressure will be higher due to the denitrification processes. Therefore, at the base of the soil zone the N_2/Ar ratio will be enhanced above the predicted 36.8 for water at 10°C; up to 43.6 where the partial pressure of N_2 is 0.92[264].

The dissolved nitrogen concentration is further enhanced by the denitrification of dissolved nitrate. The decline of the NO_3^- concentration in the suitable redox conditions, the rising N_2/Ar ratios and the isotopic fractionation observed in the $\delta^{15}N$ values of dissolved N_2 are evidence for this. The fractionation indicates a kinetic reaction which could be achieved by either a chemical or microbially mediated process.

The dissolved NO_3^- has a nitrogen isotopic ratio typical of the soil zone. Marked fluctuations in the concentrations of the NO_3^- were observed between 1976 and 1978 (figure 5.10) but the minimum concentration line was constantly maintained. Nitrate accumulated in the soil zone during the

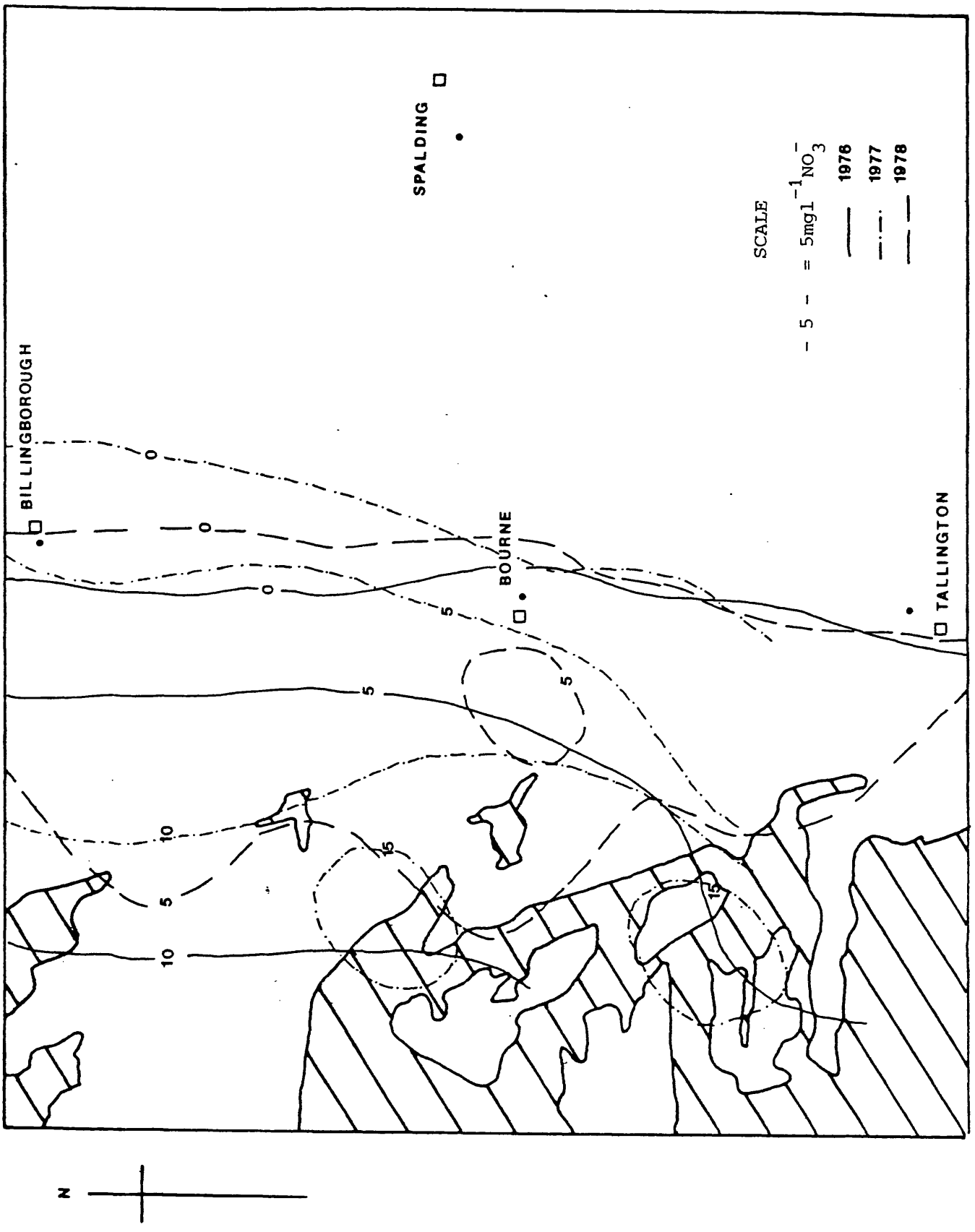


FIGURE 5.10 DISSOLVED NO_3^- CONCENTRATIONS OF LINCOLNSHIRE LIMESTONE GROUNDWATERS 1976-1978[227]

drier than average years of the early 1970's and in the drought of 1976, because the moisture conditions did not facilitate denitrification. During the autumn of 1976 recharge was abnormally high and flushed the NO_3^- into the aquifer. By 1978 a steady state was recreated with denitrification occurring in the soil zone so that low NO_3^- charged water again reached the aquifer.

The maintenance of NO_3^- free water to the east of Bourne suggested that denitrification was controlled by the chemical environment which also remained relatively constant[12]. A dilution process was discounted since the areal distribution of NO_3^- concentrations did not reflect the irregular karstic groundwater flow patterns. The occurrence of an anaerobic species of denitrifying bacteria, and the presence of NO_2^- at Lenton was evidence for the process of microbial denitrification. However, the simultaneous decline of NO_3^- and O_2 showed that anaerobic conditions, a prerequisite for microbial denitrification had not been achieved. An anoxic environment was maintained within the intergranular waters, and this would prove a suitable site for denitrification. Exchange by molecular diffusion of ionic constituents between pore water and fissure water, as observed for the Chalk, could also account for the decline of NO_3^- with subsequent denitrification.

Molecular nitrogen was converted to NH_4^+ as shown by the heavier isotopic ratio of dissolved nitrogen at Deeping RAC where NH_4^+ was recorded. The transformation process favoured the conversion of the lighter atoms. In the deep aquifer the highest concentration of NH_4^+ was recorded at Gosberton (0.587 mgl^{-1}) and would have been produced by the reduction of 2.02 mgl^{-1} NO_3^-; a typical input from an undisturbed ecosystem in the area of recharge. NH_4^+ occurs in the connate pore water and is diluted by fissure water as illustrated by the dilution mixing line drawn against chloride (figure 5.11). This shows that in the deepest parts of the aquifer, the groundwater moves at a very slow rate and there is time for the fissure water to equilibrate by molecular diffusion with the pore waters. The pore water NH_4^+ has also been

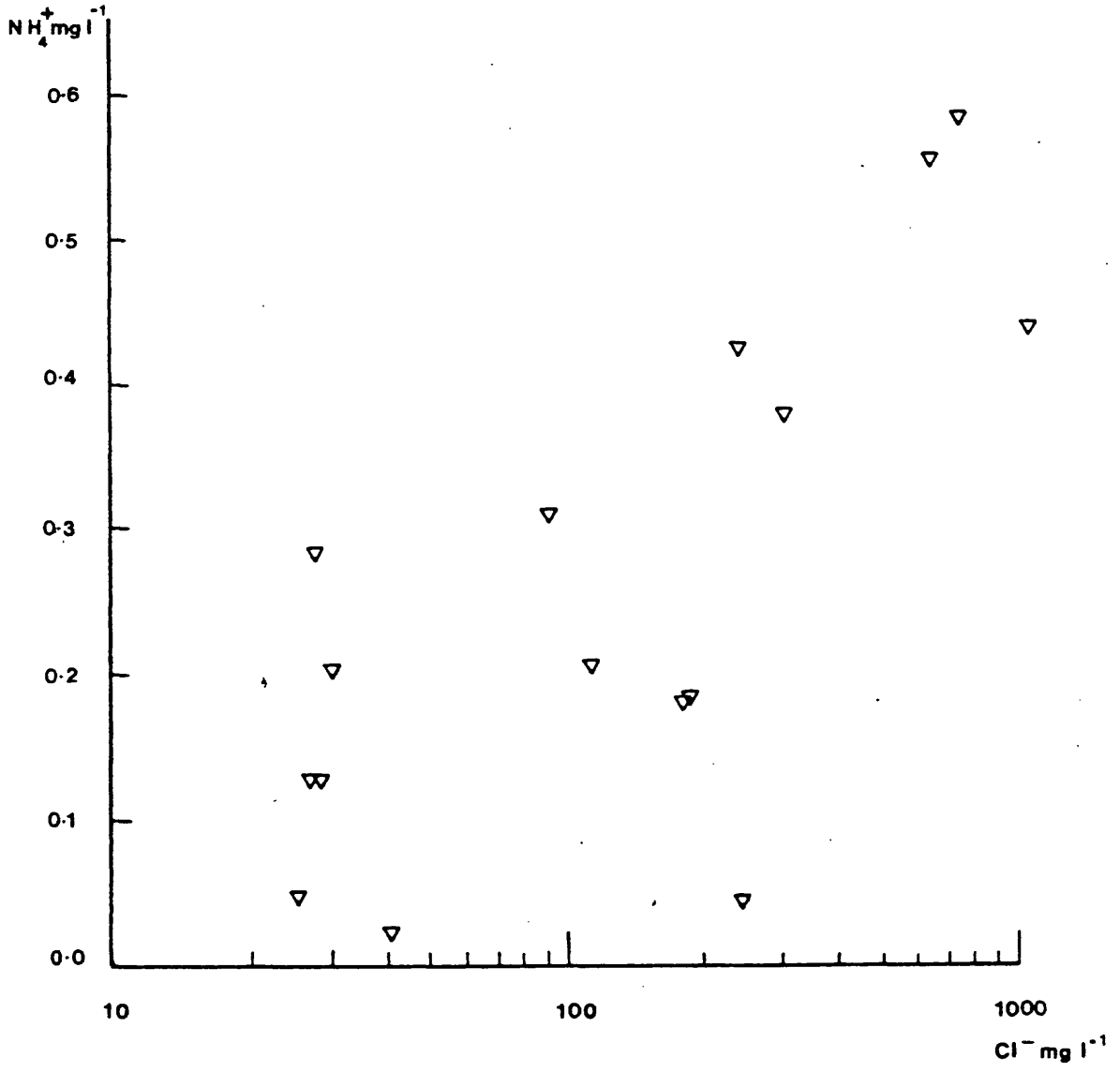


FIGURE 5.11 RELATIONSHIP BETWEEN NH_4^+ AND Cl^- IN THE LINCOLNSHIRE LIMESTONE GROUNDWATERS

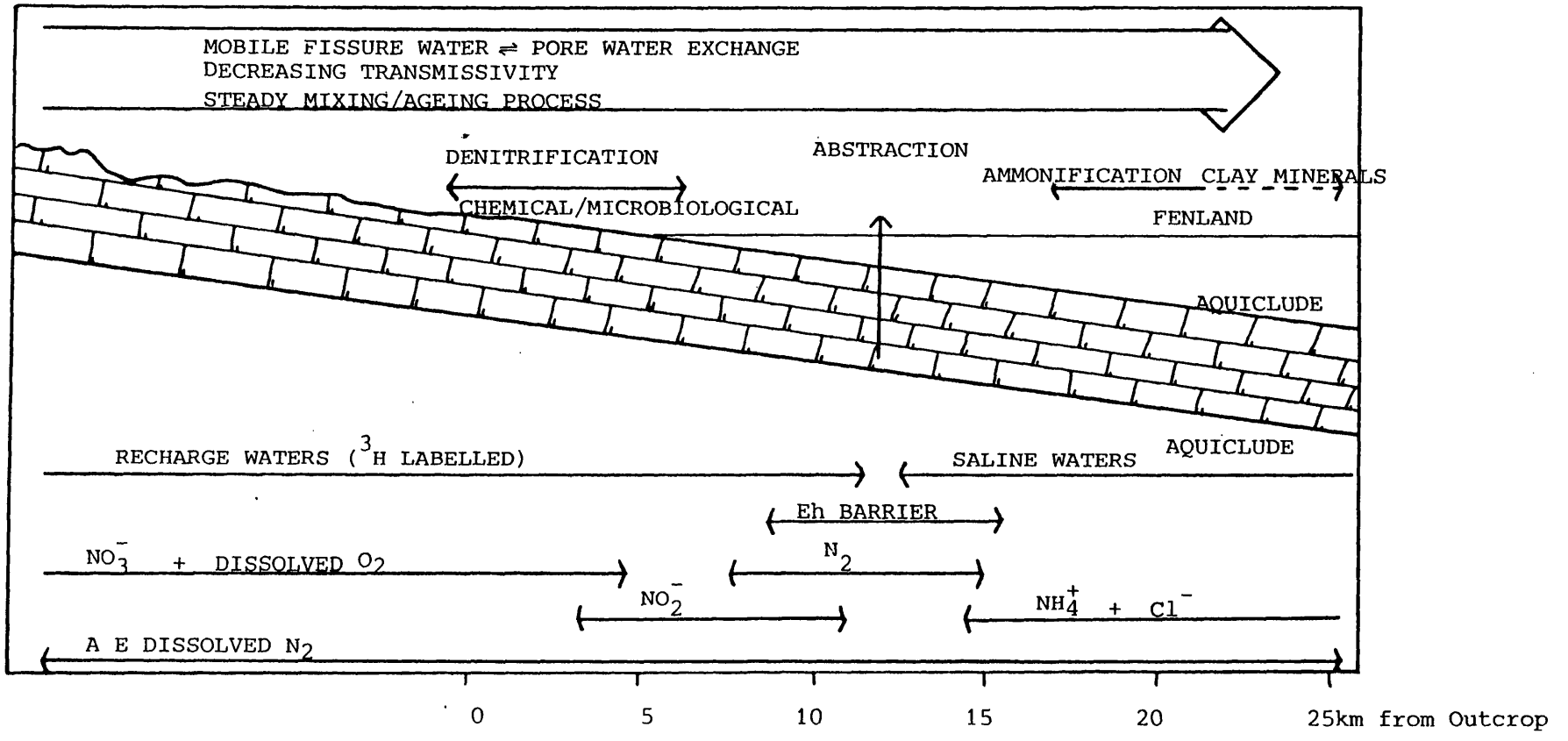


FIGURE 5.12 A SCHEMATIC SECTION OF THE LINCOLNSHIRE LIMESTONE SHOWING THE DOMINANT ZONES OF NITROGEN SPECIES AND THE AREAS IN WHICH THE TRANSFORMATION PROCESSES OPERATE

produced by the reduction of nitrogen in organic matter and dissolved N_2 from the original seawater trapped within the sediments. The combined sources of ammonia result in concentrations that are thought to be depleted by cation exchange processes involving clay minerals, so underpredicting the original nitrogen input.

In conclusion, the nitrogen hydrogeochemistry of the Lincolnshire Limestone is controlled by the oxidation-reduction environment. Denitrification occurs by the exchange of mobile fissure water with static pore water, and the subsequent denitrification by microorganisms in the anaerobic environment of the rock pores. The advance of the high nitrate water is contained by this natural transformation process, and by the pattern of water abstraction acting as an effective barrier to movement of modern recharge water to the deep aquifer.

The nitrogen hydrogeochemical cycle of the Lincolnshire Limestone is summarised in figure 5.12.

5.3 THE BERKSHIRE CHALK

5.3.1 A REVIEW OF THE HYDROGEOLOGY

The study area of the Berkshire Chalk comprised a transect from outcrop in the Lambourn Valley to the Chalk confined beneath about 100m of tertiary deposits, south of Reading (figure 5.13). The Chalk forms the largest aquifer in England, and its properties vary locally according to structure and lithology. In Berkshire the Chalk forms the western end of the easterly plunging London Basin Syncline; a large asymmetric fold with dips[228] of between 1° and 3° (figure 5.14). The stratigraphic sequence is outlined in Table 5.11 and the maximum thickness of Chalk exceed 240m. Groundwater flow

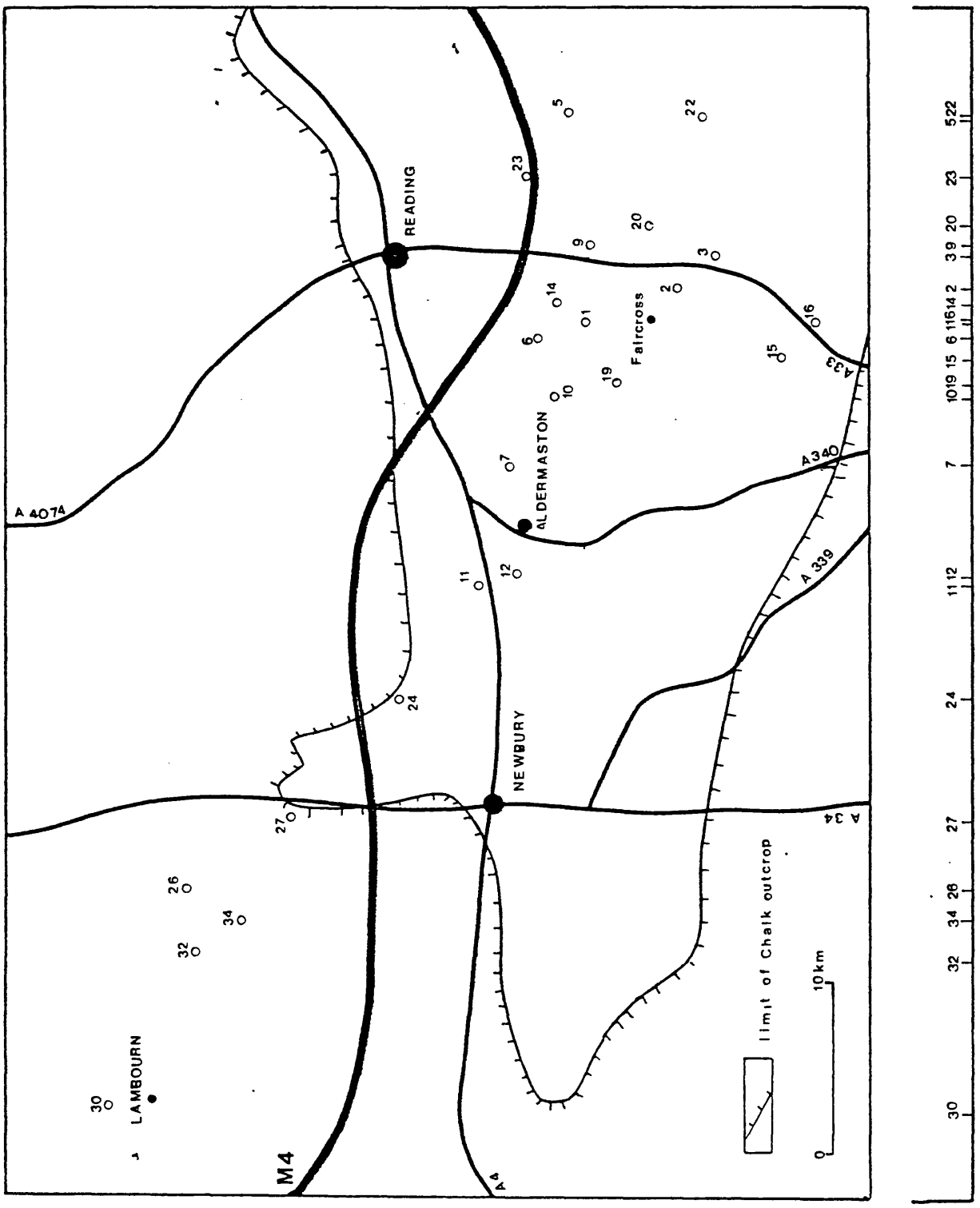


FIGURE 5.13 LOCATION MAP AND SECTION OF BOREHOLES SAMPLED ON THE BERKSHIRE CHALK

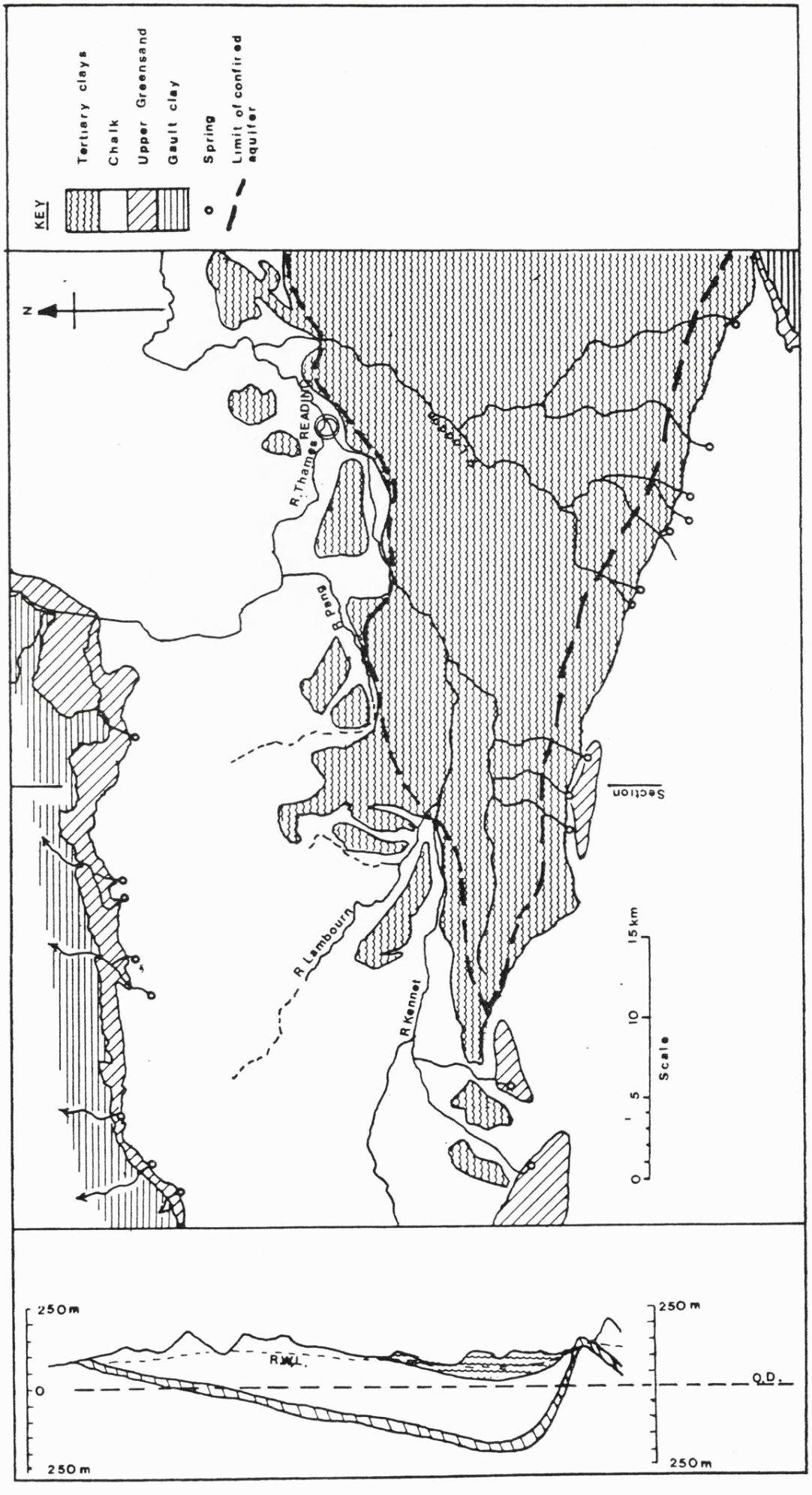


FIGURE 5.14 GEOLOGICAL MAP AND SECTION OF THE STUDY AREA[244]

TABLE 5.11 LIST OF FORMATIONS[244]

		Formation	Sub-division	Thickness m.	Principal Rock Type	Hydrogeological Classification
Drift Formations	Holocene and Pleistocene	Alluvial clay		0–1	Silty clay	
		Valley gravel		0–6	Gravel and sand	
		Plateau gravel		0–3	Clayey gravel	
		Clay-with-flints		0–10	Clay, sand, gravel	
		Coombe deposits		0–3	Chalk debris	
Solid Formations	Unconformity					
	Eocene	Bagshot Beds		30	Fine sand, clay	Minor Aquifer
		London Clay		45–90	Clay	Aquiclude
		Reading Beds		20–25	Clay, sand, silt	
	Unconformity					
	Cretaceous	Chalk	Upper Chalk	75–110	White Chalk (with flint)	Major Aquifer
			Middle Chalk	45–60	White and buff Chalk (no flint)	
			Lower Chalk	50–85	Buff and Grey Chalk (no flint)	
		Upper Greensand		15–30	Silty Sand and Sandstone	
		Gault		65–70	Clay and silty clay	Aquiclude

takes place predominantly within the uppermost 50m of the saturated zone[229].

The Chalk is a soft white micritic limestone, comprised of microfossil debris 0.2 to 3.0mm in size. It is almost entirely calcium carbonate[230,231], but with some fine grained insoluble residues[232]. Bands of flints occur in the Upper Chalk, while in the Middle and Lower Chalk a higher clay mineral content is found.

The aquifer properties of the Upper and Middle Chalk have been determined at Winterbourne near Newbury, Berkshire[235]. The values of both vertical and horizontal intrinsic permeabilities are very low. However, the bulk permeability was estimated at 37,000 millidarcys. This discrepancy between intergranular and bulk measurements demonstrates that movement and active storage in the Chalk takes place mainly through the interconnected fissure system[234]. The observed transmissivity at Winterbourne was $2830m^2/d$, but in general the values are lower (figure 5.15). The Chalk has a high porosity with pore diameters generally less than $5\mu m$[4], and an interstitial specific surface area of $60,000cm^2$ per cm^3 pore volume[233]. Thus, there is a high surface area for water-rock interaction.

Recharge to the area is principally by precipitation and through the beds of rivers such as the Lambourn. The maximum rainfall occurs over the Chalk hills and is about 740mm/year, whilst the mean potential evaporation is in the order of 520mm/year. The average annual recharge to the Chalk aquifer at outcrop ranges from 200 to 425mm/year. Abstraction from public supply boreholes averages 90×10^3 m^3/d and abstraction for irrigation amount to 10×10^5 m^3/d. Approximately 10% of the average recharge is abstracted[229].

Recharge of the saturated Chalk aquifer is by rapid transit of water in macrofissures (>2mm effective width)[234], and by a process analagous to piston displacement in microfissures (<2mm effective width)[235,236].

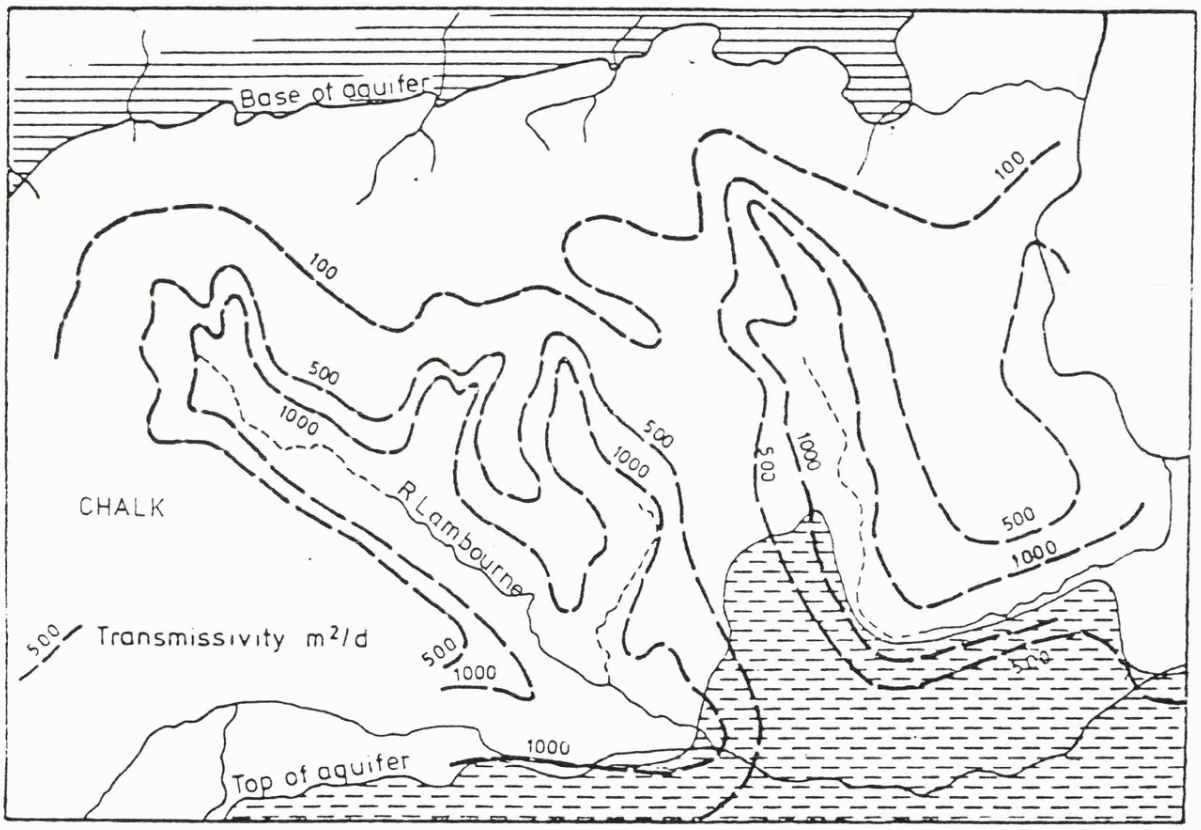


FIGURE 5.15 TRANSMISSIVITY OF THE CHALK AROUND THE LAMBOURNE VALLEY[244]

Dissolved ions are able to diffuse from the water in the macrofissures to the microfissure water and into the rock matrix[237,238] and are then stored in the interstitial pore waters. The Chalk acts as a chromatographic column[4] with the water being quickly eluted while the dissolved ions are gradually separated as they move down the unsaturated zone. About 10-15% of the infiltration entering the Chalk moves directly through the major fissures to the saturated zone without significant interaction with the rock matrix[239,240]. Rapid infiltration occurs after storm events, with the water moving through the major fissures. Infiltration moving slowly through microfissures diffuses into the matrix; the rate of movement, dependent upon the physical rock characteristics, determines the water residence time and thus the composition. The slower the flow rate , the more nearly will the fissure water equilibrate with the pore water. The pore water has been shown elsewhere in the Chalk to be connate in origin[241].

The hydrogeochemistry of the Berkshire Chalk is very similar to that of the Chalk of the London Basin[228]. Several stages can be recognised in a sequence of chemical changes as the groundwater flows to the confined aquifer where circulation is restricted. These stages have been described for the Chalk, including part of the London Basin, and 5 zones of different water quality identified[48]. The principal features of these zones are summarised.

Zone 1 Outcrop area where solution reaction predominates.

Zone 2 The shallow confined area where again solution predominates. Carbonate hardness and non-carbonate hardness rise to a maximum value. The downdip limit is marked by a maximum value for HCO_3^-.

Zone 3 The HCO_3^- decreases to a minimum associated with precipitation of alkaline earth carbonates.

Zone 4 A zone of very soft water. Carbonate hardness is dominant. Ion

exchange processes govern the groundwater chemistry and sodium is the principal cation. The bicarbonate content and alkalinity increase in this zone.

Zone 5 Saline water dominated by Na^+ and Cl.

The fifth zone of saline water is not represented in the Chalk of Berkshire where the normal value of Cl^- does not exceed $150mgl^{-1}$.

5.3.2 THE BERKSHIRE CHALK HYDROGEOCHEMICAL SURVEYS 1979 AND 1982

The hydrogeochemistry of the Berkshire Chalk was studied with particular reference to NO_3^- along a section trending south-east from the Lambourn Downs to the confined aquifer south of Reading. The results of the surveys have been plotted on one section which follows the major groundwater flow line of the Chalk aquifer.

A total of 24 boreholes were investigated. These wells penetrated to various depths, drawing water from the different zones of the Chalk. The hydrogeochemistry in part reflected this mixture, but since the major portion of the well waters was derived from the upper 50m of the Chalk a change in water quality downdip was observed.

The Physico-Chemical Groundwater Environment

At each site, the physico-chemical parameters were measured (Table 5.12). The pH value averaged 7.0 at outcrop, and gradually rose to 7.5 at about 15km from outcrop (figure 5.16). A marked drop of 300-400mV in the Eh value was observed within a few kilometres of the confinement of the Chalk. Dissolved oxygen followed a similar trend, and was reduced to trace values in

TABLE 5.12 THE PHYSICO-CHEMICAL PARAMETERS OF THE BERKSHIRE CHALK GROUNDWATERS, 1979

SITE NO	NAME	G R	TEMP ^{0}C	pH	Eh.mv	Dis O_2 mgl^{-1}
1.	Missels Bridge	69356529	12.8	7.45	50.0	0.45
2.	Standford End	70746285	12.8	7.55	80.0	0.25
3.	Lawn Farm	69986011	14.8	7.64	40.0	0.40
6.	Grazeley	68696801	12.8	7.45	80.0	0.80
7.	Ufton Nervet	62326824	12.8	7.10	04.0	0.40
9.	Dairy Research Inst.	72956828	12.8	7.45	40.0	0.40
11.	Woolhampton	5708664	12.5	7.10	60.0	0.40
12.	Old Mill Hotel	59096624	12.8	7.20	05.0	0.30
14.	Grazeley Court Fm	693674	14.0	7.60	50.0	0.30
15.	Shalford Fm	56926415	12.4	7.10	50.0	0.35
16.	Sherfield Manor	681571	12.9	7.25	110.0	0.45
18.	Redlands	66985545	12.0	7.15	90.0	0.30
19.	Little Park Farm	67916307	13.6	7.45	90.0	0.00
20.	Wellington Park	729626	13.6	7.35	30.0	0.35
22.	Well House	75366313	18.0	7.65	-50.0	0.30
23.	Shinfield Stn	73466854	17.4	7.45	60.0	0.00
24.	Cold Ash	50247040	11.6	7.05	415.0	6.90
26.	Brightwalton	42577940	11.5	6.95	390.0	8.50
27.	Chieveley	47637515	11.2	7.15	415.0	8.20
30.	Mile End	33138109	10.4	7.25	355.0	9.80
32.	Henley Farm	39857801	10.6	7.10	335.0	9.80
34.	RAF Welford	41977581	11.3	6.95	370.0	9.00

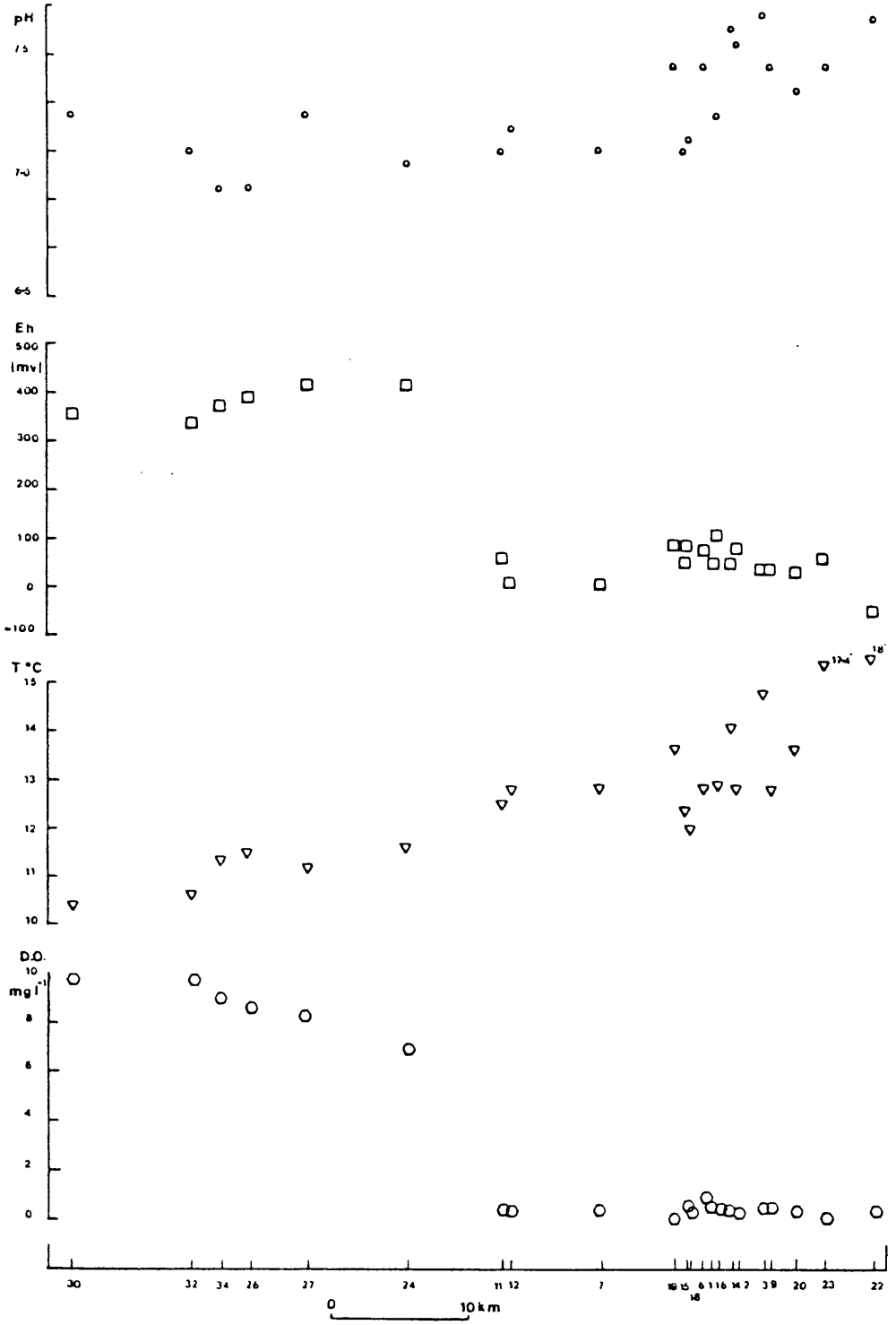


FIGURE 5.16 THE PHYSICO-CHEMICAL PARAMETERS OF THE BERKSHIRE CHALK GROUNDWATERS, 1979

the confined environment.

Dissolved Ionic Nitrogen Species and Chloride

The ionic species of nitrogen and chloride were determined for each site (Table 5.13). The NO_3^- concentrations averaged $21mgl^{-1}$ at outcrop with the highest value recorded at Cold Ash ($32.49mgl^{-1}$). Downdip, nitrate concentrations decreased to trace quantities and the disappearance of NO_3^- was coincident with the decline in dissolved oxygen (figure 5.17). With the onset of reducing conditions NO_2^- was observed in two distinct areas on either side of the deep confined groundwater region. Ammonium was first detected where the trace NO_3^- values occurred. The concentration increased and the highest value of $1.09mgl^{-1}$ was recorded at Lawn End, in the centre of the area of more saline water. A similar pattern was observed for the Cl^- concentrations.

Inert Gases and Recharge Temperatures

The groundwaters were analysed for dissolved gases (^4He, Ne, Ar, Kr, Xe and N_2) using Stable Isotope Dilution Analysis in 1979. From the concentration of these gases, the recharge temperatures were computed by calculating the quantities of inert gases in the groundwaters and relating them by a solubility equation[41] to the temperature at which they dissolved. The quantity of dissolved Ar, for example, is given by

$$[Ar] = S_T P_{Ar} \ (cm^3 \ STP \ cm^{-3} \ H_2O)$$

where S_T is the solubility of Ar at 1 atm pressure and the temperature of recharge T; and P_{Ar} is the partial pressure of Ar in the atmosphere. Similar relationships apply to the other inert gases. Gas solubilities decrease with increasing temperature but any increase in the aquifer will not

TABLE 5.13 THE NITROGEN SPECIES AND CHLORIDE ION CONCENTRATION OF BERKSHIRE CHALK GROUNDWATERS, 1979

Site	Name	$NO_2 mgl^{-1}$	$NO_3 mgl^{-1}$	mgl^{-1} NH_4^+	$Cl^- mgl^{-1}$
1.	Missels Bridge	0.000	0.01	0.57	96.0
2.	Standford End	0.014	0.06	0.95	183.0
3.	Lawn Farm	0.004	0.03	1.09	204.0
6.	Grazeley	0.000	0.12	0.53	78.0
7.	Ufton Nervet	0.000	0.12	0.05	27.0
9.	Dairy Research Inst.	0.000	0.03	0.90	129.0
11.	Woolhampton	0.000	0.00	-0.01	20.0
12.	Old Mill Hotel	0.000	0.12	0.08	16.0
14.	Grazeley Court Fm	0.000	0.01	0.81	101.0
15.	Shalford Fm	0.000	0.01	-0.01	16.0
16.	Sherfield Manor	0.014	0.07	0.33	21.0
18.	Redlands	0.000	0.04	0.10	170.0
19.	Little Park Farm	0.000	0.12	0.69	30.0
20.	Wellington Park	0.000	0.00	0.64	66.0
22.	Well House	0.004	0.42	0.60	55.0
23.	Shinfield Stn	0.001	0.12	0.89	117.0
24.	Cold Ash	0.000	32.49	-0.01	23.0
26.	Brightwalton	0.000	18.72	-0.01	9.0
27.	Chieveley	0.000	24.55	-0.01	18.0
30.	Mile End	0.000	21.58	-0.01	13.0
32.	Henley Farm	0.000	21.58	-0.01	12.0
34.	RAF Welford	0.000	19.72	-0.01	18.0

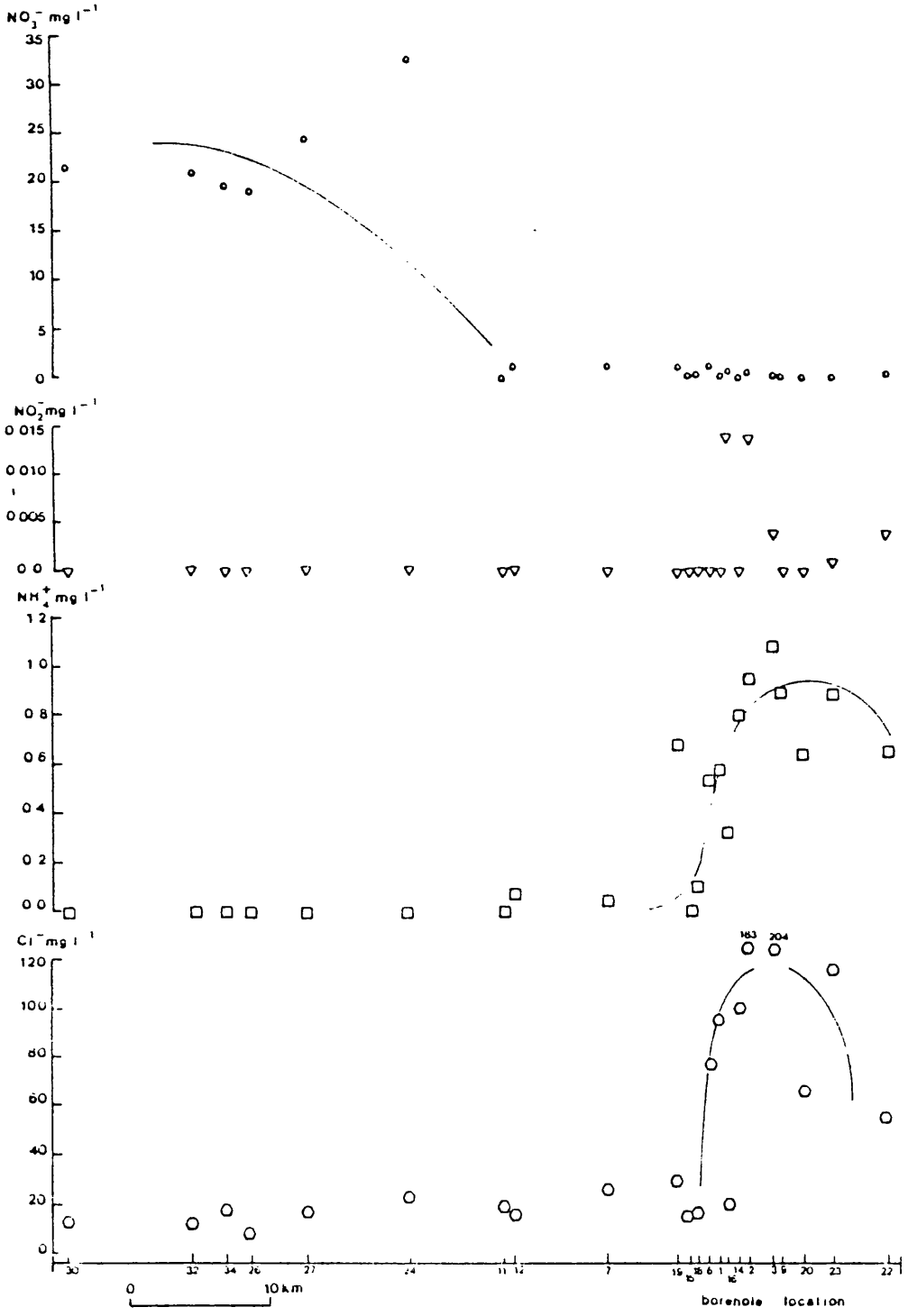


FIGURE 5.17 THE DISTRIBUTION OF NITROGEN SPECIES AND CHLORIDE IN THE BERKSHIRE CHALK GROUNDWATERS, 1979

result in gas exsolution since the increased hydrostatic pressure maintains the groundwater undersaturated with respect to the gases. It is therefore valid to derive recharge temperatures from the inert gas contents (Table 5.14). A trend of lower recharge temperature with increased depth into the confined zone was found for the Berkshire Chalk (Table 5.15), (figure 5.18a).

Radiogenic Helium

Excess radiogenic ^4He contents (the excess of dissolved ^4He over the amount dissolved from the atmosphere at recharge temperature) were calculated (Table 5.16). The excess ^4He contents were plotted against the Cl^- content, and used here as a rough index of groundwater residence time, since the concentration of both elements is dependent on rock/water interaction. The excess ^4He content increased linearly with increasing chlorinity, (figure 5.19).

The N_2/Ar Ratio

N_2/Ar ratios in 1979 were derived by calculation from the absolute concentration of gases. In 1982 the ratios were determined on samples collected in evacuated $250cm^3$ glass bottles. Replicate samples for each site showed great variation (Table 5.14) attributed to contamination by atmospheric air, and excess air in the samples. Nevertheless, the results do clearly demonstrate two distinct groups of ratios (figure 5.20). Those values with an N_2/Ar ratio greater than 62 are considered to be contaminated. The second group shows a probable trend of increasing N_2/Ar ratios towards the redox boundary, reaching a maximum of 47 at the boundary itself. This would result from the denitrification of the present NO_3^- input ($21mgl^{-1}$) at a recharge temperature of 10°C. At Little Park Farm some confidence is

TABLE 5.14 INERT GAS CONTENTS AND N_2/Ar RATIOS FOR THE GROUNDWATERS OF THE BERKSHIRE CHALK, 1979

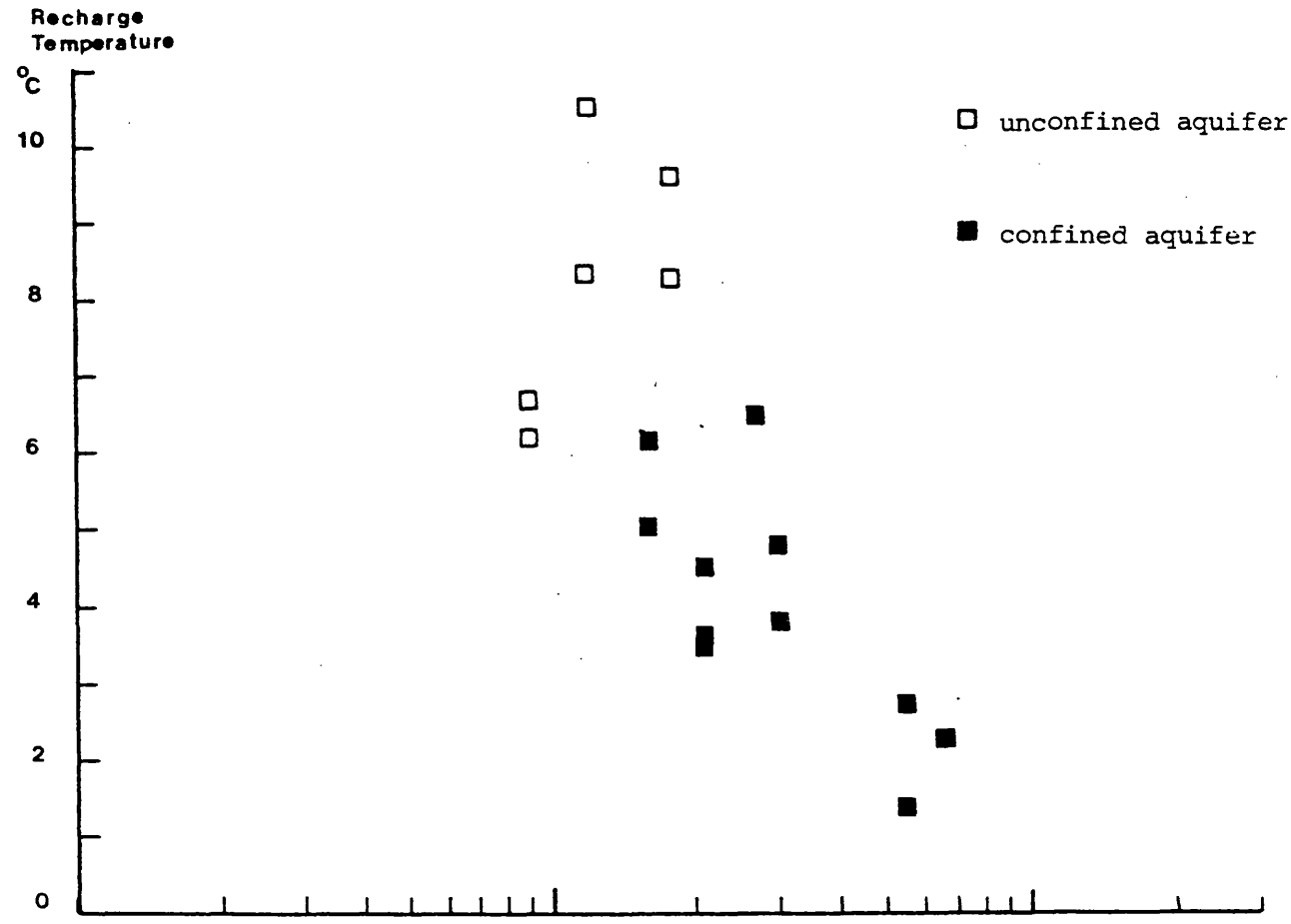
No.	Site Name	Dissolved Gas Content in cm per cm ^3H_2O						
		$Hex10^{-7}$	$Nex10^{-7}$	$Arx10^{-4}$	$Xex10^{-8}$	N_2x10^{-2}	N_2x10^{-2}	N_2/Ar
7.	Ufton Nervet	2.82	2.2	3.17	1.03	1.38	1.21	41.68
9.	Dairy Research	0.66	2.2	4.64	1.00	1.25	1.66	41.58
	Inst	89.45	2.2	17.06	-	-	-	-
12.	Old Mill Hotel	2.68	2.2	4.51	1.04	1.93	1.91	45.08
		-	2.2	4.40	1.00	1.14	1.88	46.72
16.	Sherfield Manor	6.91	2.2	4.58	1.08	1.15	1.75	41.55
		-	2.2	4.66	1.11	1.17	1.69	39.54
		8.33	2.2	4.66	7.20	1.74	1.74	40.15
18.	Redlands	3.42	2.2	4.59	1.05	1.85	1.86	51.67
19.	Little Park Farm	4.80	2.2	4.61	1.09	2.52	2.01	46.55
		8.83	2.2	4.54	1.15	-	1.93	46.81
20.	Wellington Park	12.40	2.2	4.76	1.10	-	1.80	40.80
22.	Well House	-	2.2	4.87	1.15	1.54	1.48	35.48
		7.52	2.2	4.91	1.14	7.67	1.81	40.63
23.	Shinfield Stn	1.90	2.2	4.17	1.10	1.10	1.82	48.68
26.	Brightwalton	-	2.2	4.40	0.98	1.91	1.56	38.45
		0.65	2.2	4.32	0.97	1.06	1.63	42.00
27.	Chieveley	1.99	2.09	4.74	0.83	1.28	1.61	33.95
		1.59	2.2	4.18	0.98	1.30	1.50	40.46
32.	Henley Farm	0.65	2.2	4.02	0.91	-	1.52	41.59
		0.51	2.2	4.18	0.96	3.24	1.58	40.74
30.	Mile End	1.05	2.2	3.93	0.75	1.03	7.21	15.61
34.	RAF Welford	0.39	2.2	4.0	0.94	1.10	1.63	43.92

Analyses with Ne contents greater than $2.2x10^{-7}$cm per cm ^3H_2O and with N_2/Ar ratios greater than 62 have been omitted due to contamination by atmospheric and excess air.

TABLE 5.15 RECHARGE TEMPERATURES FOR THE GROUNDWATERS OF THE BERKSHIRE CHALK

No	SITE NAME	TEMPERATURE °C
7	Ufton Nervet	6.5
12	Old Mill Hotel	6.2
16	Sherfield Manor	3.5 3.6 4.5
19	Little Park Farm	3.8 4.8
20	Wellington Country Park	2.3
22	Well House	1.4 2.8
26	Brightwalton	6.2 6.7
27	Chieveley	8.3
32	Henley Farm	8.3 10.5
34	RAF Welford	9.6

a)



b)

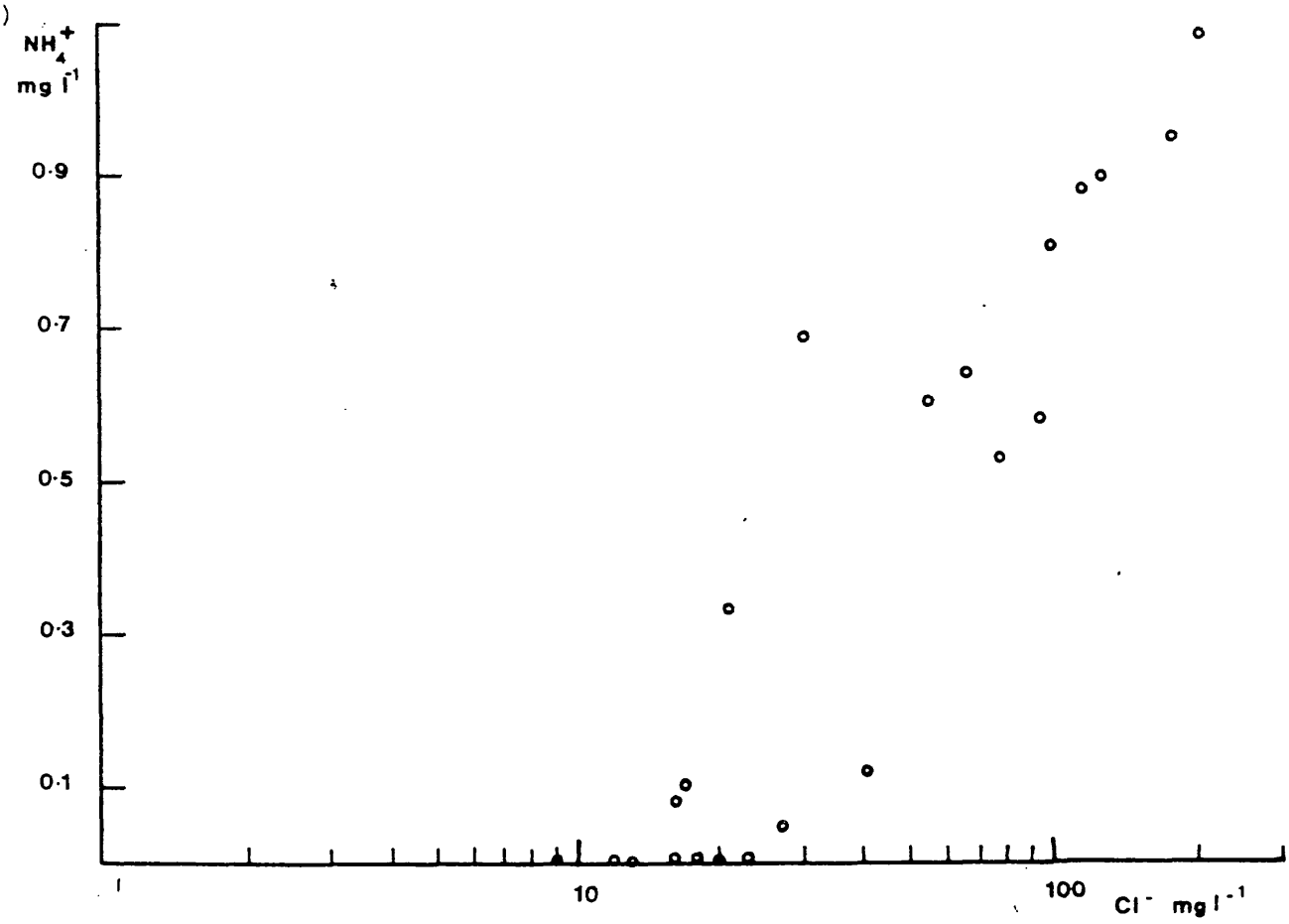


FIGURE 5.18 a) RECHARGE TEMPERATURE AGAINST Cl^- CONTENT

b) NH_4^+ CONCENTRATION AGAINST CL^- CONTENT FOR THE BERKSHIRE CHALK GROUNDWATERS

TABLE 5.16 EXCESS ^{4}He CONTENT OF THE BERKSHIRE CHALK GROUNDWATERS

NO	SITE NAME	EXCESS ^{4}He cm^{3} STP cm^{-3} H_2O x 10^{-7}
7	Ufton Nervet	2.34
		2.57
12	Old Mill Hotel	2.20
16	Sherfield Manor	6.42
		7.84
19	Little Park Farm	4.32
		8.35
20	Wellington Country Park	11.91
22	Well House	0.91
26	Brightwalton	0.17
27	Chieveley	1.52
		1.12
32	Henley Farm	0.18
		0.04
34	RAF Welford	-0.08

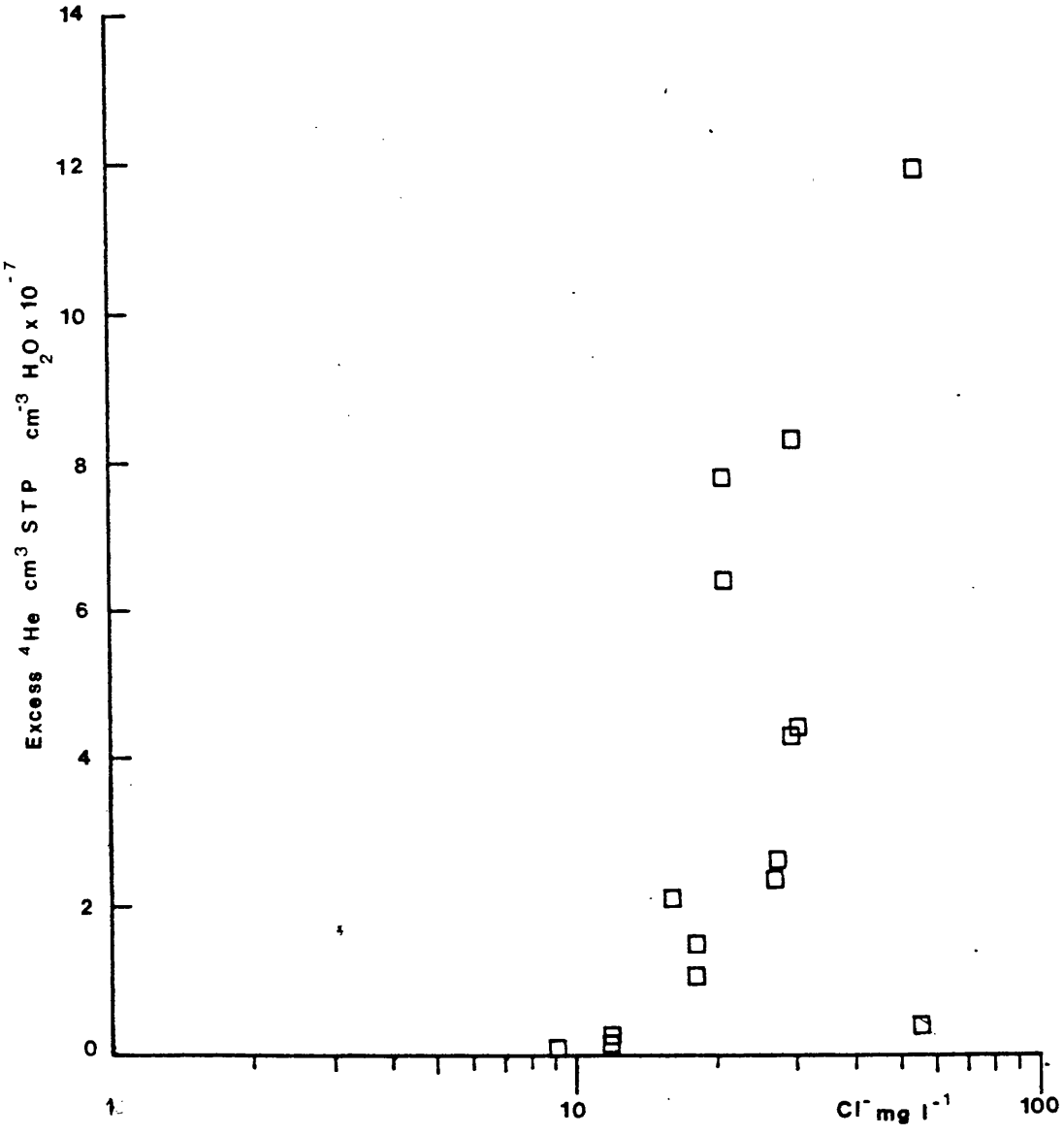


FIGURE 5.19 EXCESS ^{4}He CONTENT OF THE BERKSHIRE CHALK GROUNDWATERS PLOTTED AGAINST CHLORIDE ION CONTENT

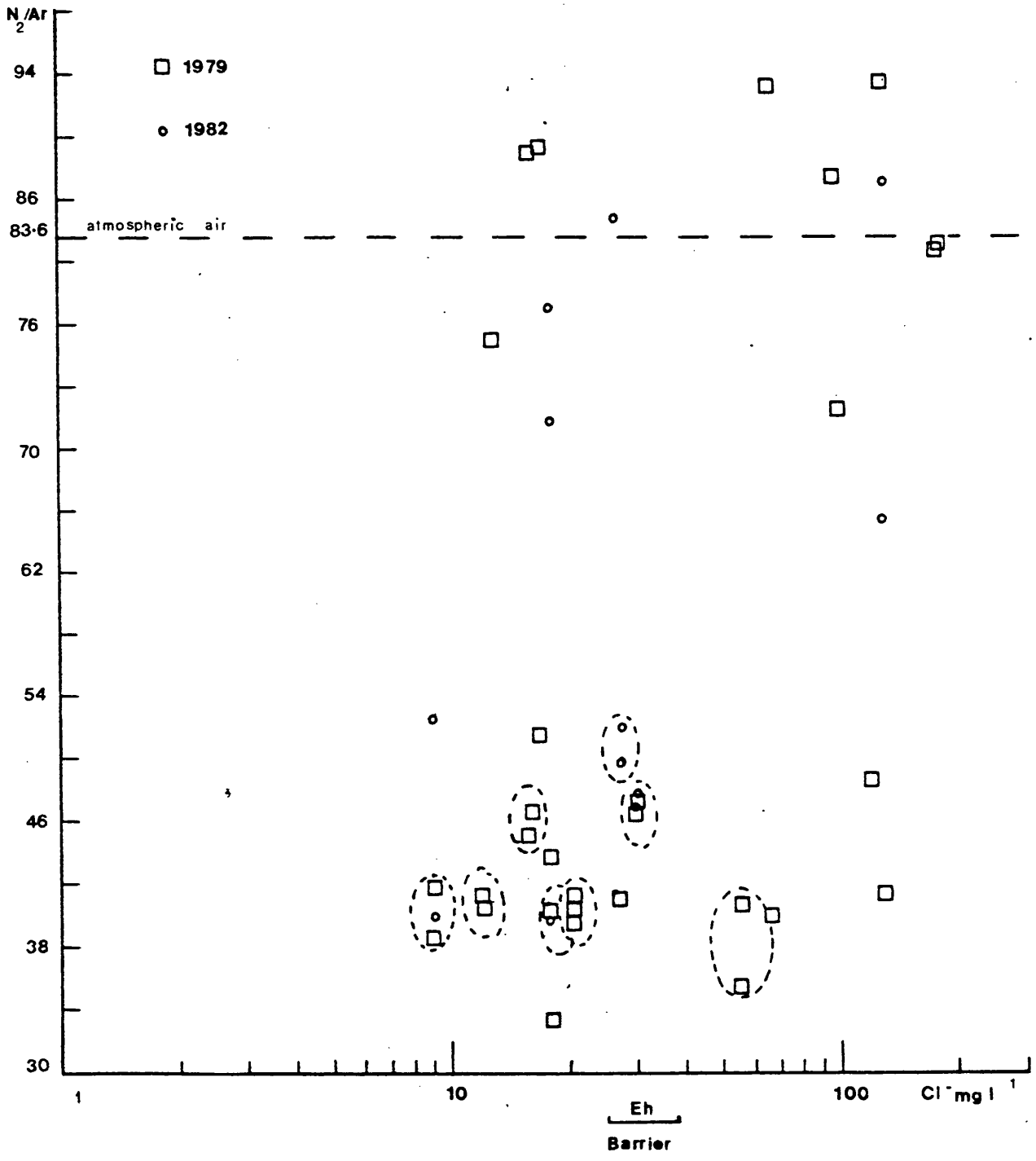


FIGURE 5.20 THE N_2/Ar RATIO OF THE BERKSHIRE CHALK GROUNDWATERS, 1979 AND 1982

given to this interpretation, for this is the only site where good reproducibility of the N_2/Ar ratio was found in both 1979 and 1982, and determined at 46.7 ±0.2. A comparison of the results for these years (Table 5.17) shows close agreement between the mean values of the two outcrop sites at Brightwalton and Chieveley. There is no evidence for further increase in N_2/Ar beyond the redox boundary.

The $\delta^{15}N$ of Dissolved Nitrogen

The $\delta^{15}N$ values of the dissolved N_2 (Table 5.17) were excessively enriched above the expected natural range of groundwater, and even higher than for artificial fertilizers. These results are considered to be invalid due to contamination by an unknown source during preparation for analysis.

5.3.3 DISCUSSION OF THE RESULTS OF THE HYDROGEOCHEMICAL SURVEYS OF THE BERKSHIRE CHALK

Nitrate

The behaviour of nitrogen in the Berkshire Chalk is again largely controlled by the redox environment. NO_3^- is the dominant nitrogen species at outcrop with a mean value of $21 mgl^{-1}$ and its eastward limit is very clearly defined by the onset of reducing conditions. The high value observed at Cold Ash must indicate a source of pollution. The decline in the Eh value is coincident with the fall in the NO_3^- and O_2 values.

In this aquifer the concentration of nitrate in the groundwater is very much dependent on the type of flow. The high nitrate content of recharge water is rapidly diluted by the low nitrate content stored water in the major fissures of the upper 50m of Chalk in the unconfined aquifer.

TABLE 5.17 N_2/Ar RATIOS AND $\delta^{15}N$ FOR DISSOLVED N_2 IN THE BERKSHIRE CHALK GROUNDWATERS 1982

NO	SAMPLE		$\delta^{29}/_{28}$ o/oo	$2\sigma_{10}$	$\delta^{29}/_{40}$ o/oo	$2\sigma_6$	$^{29}/_{40}$	N_2/Ar
7	Ufton Nervet	1.	46.53	0.05	34.14	0.61	0.6292	84.684
		2.	47.37	0.02	-391.05	0.30	0.3705	49.865
		3.	50.86	0.02	-364.63	0.84	0.3865	52.018
9	Dairy Research Institute	1.	3.21	0.13	-196.29	2.07	0.4890	65.811
		2.	7.23	0.09	61.68	3.39	0.6459	86.935
19	Little Park Farm	1.	29.65	1.223	-429.26	3.66	0.3472	46.735
		2.	31.19	0.59	-429.36	2.31	0.3472	46.735
		3.	25.58	2.12	-402.65	2.57	0.3634	48.916
26	Brightwalton	1.	56.51	0.03	-359.79	0.66	0.3895	52.430
		2.	37.41	0.14	-457.49	0.35	0.2971	39.986
27	Chieveley	1.	16.04	0.08	-121.03	0.44	0.5348	71.973
		2.	26.60	0.01	-513.79	0.57	0.2958	39.813
		3.	3.56	0.04	- 37.47	2.30	0.5856	78.816

TABLE 5.18 A COMPARISON OF N_2/Ar RATIOS IN THE BERKSHIRE CHALK GROUNDWATERS FOR 1979 AND 1982

No	SITE NAME	N_2/Ar 1979	N_2/Ar 1982
7	Ufton Nervet	41.65	[84.68]
			49.87
			52.02
	Mean	41.68	50.94
9	Dairy Research Institute	[93.59]	[65.81]
		41.58	[86.94]
	Mean	41.58	
19	Little Park Farm	46.55	46.74
		46.81	46.74
			[48.92]
	Mean	46.68	46.74
26	Brightwalton	41.99	[52.43]
		38.45	39.99
	Mean	40.22	39.99
27	Chieveley	40.46	[71.97]
		[33.95]	39.81
			[78.82]
	Mean	40.46	39.81

[ ] N_2/Ar ratios considered to be contaminated

This is especially so in the areas of high transmissivity along river valleys (figure 5.15). However, the dilution by diffusion of NO_3^- into the stored pore water is the primary mechanism for the decreasing NO_3^- content.

Denitrification

With the onset of the confined condition, the chemical environment is such that nitrate reduction becomes possible, In the unconfined zone of the Berkshire Chalk, as in the Lincolnshire Limestone, anaerobic conditions are only present in the pore spaces of the rock matrix, and denitrification can occur within them. No microbiological data were collected in the present survey, but nitrate reducing bacteria have been identified in waters of the London Basin Chalk, north of the Thames[239]. It is probable that these bacteria are ubiquitous in the Chalk aquifer and are able to mediate the denitrification process, particularly where the pore dimensions of the Chalk are large enough to accommodate the bacteria.

Fissure Storage and the Diffusion Process

The probable rise in the N_2/Ar ratio (figure 5.20) is evidence that denitrification occurs and the peak of the dissolved N_2 content appears at Little Park Farm, some 10km beyond the redox 'barrier'. This indicates that NO_3^- is reduced to N_2, but that a lag occurs between the optimum reducing chemical environment near the barrier and the appearance of the molecular nitrogen. This may be accounted for if denitrification occurs in the interstitial water, and a reverse molecular diffusion of the product with fissure water takes place, but that equilibrium is not reached between the dissolved N_2 concentration in the pore water and fissure water until 10km deeper into the aquifer. This mechanism can also explain why NO_2^-, the intermediate product of denitrification process, does not appear until after the nitrogen peak because the diffusion coefficient of NO_2^- is probably smaller

than that for N_2. This lag effect in equilibration by diffusion processes is not observed in the Lincolnshire Limestone because the pore sizes of the latter are much greater.

Origin of Nitrogen Species in the Deep Aquifer

As the chemical environment becomes more reduced with depth into the aquifer, NH_4^+ becomes the dominant nitrogen species. The nitrogen in this area is mostly derived from equilibration with the soil air at recharge, but some originates from the gas dissolved in connate stored water. The nitrogen is in a metastable state and is eventually reduced to NH_4^+. Other nitrogen species in recharge waters, and also species derived from the sediments are reduced through molecular nitrogen to NH_4^+. The occurrence of old saline water is shown by the increase in the Cl^- content, and above $50mgl^{-1}$ Cl^- a straight line relationship with NH_4^+ exists, as in Lincolnshire (figure 5.18b). This indicates an accumulation of NH_4^+ with time, for the present NO_3^- ($21mgl^{-1}$ NO_3^-) and N_2 ($0.014cm^3cm^{-3}$ at 10°C) recharge inputs reduce to 27 times the peak NH_4^+ ($1.09mgl^{-1}$) value. The past temporal variation in NO_3^- levels are unknown but this estimate more than accounts for the present levels of ammonium, and even if the NO_3^- input were reduced to $10mgl^{-1}$, recharge NO_3^- could still be cited as the main source of NH_4^+.

The origin of the NH_4^+ can only be a semi-quantitative measure since the cation preferentially exchanges with Na^+ on clay surfaces[262,263]. The total accumulation of ammonium cannot be calculated, and so the contribution of connate nitrogen species cannot be estimated, but it is probably not significant.

Recharge Temperature and Groundwater Origin

The recharge temperature also shows a linear relationship with the Cl^-

content (figure 5.18a) as does the ^{4}He concentration (figure 5.19). The helium relationship points to a steady ageing or mixing process occurring across the aquifer. The oldest waters in the aquifer have been ^{14}C dated at 10,000 years[240]. This correlates with the end of the Devensian glaciation[135]. Recharge prior to this would be unlikely to have occurred because of permafrost. Following the last glacial advance the climate steadily moderated and about 5000 to 7000 years BP the highest post glacial temperatures were attained[242]. The recharge temperatures show a progressive decrease with distance from outcrop, reaching 1°C in the deep groundwaters. Post Devension recharge temperatures have not been found below 8°C[262], so the Berkshire Chalk groundwaters are not derived from meteoric recharge but from permafrost meltwater Thus the groundwaters with the lowest recharge temperatures result from air equilibrated meltwater passing rapidly through the cryoturbated soil, and frost fractured upper horizons of the Chalk.

With amelioration of the climate, the recharge temperatures would have increased, and followed the trend of fluctuating post glacial air temperatures[243]. However, this was not observed and the straight line relationship between recharge temperature and Cl^- suggests a process whereby the recharge of permafrost meltwaters stored in the intergranular spaces mix with modern recharge carried in the fissures. This process is exemplified in the aquifer half way between the recharge area and the deep confined zone, where a recharge temperature of 4.5°C was measured with an N_2/Ar ratio indicative of a modern NO_3^- input of $21 mgl^{-1}$ suggesting mixing of 50% recharge with 50% stored groundwater.

Summary

In the Berkshire Chalk, after initial denitrification in the soil zone, the average concentration of NO_3^- leached to the unsaturated groundwaters is $21 mgl^{-1}$. As the Cl^- content increases and the aquifer becomes confined, the

nitrate level decreases. At the redox barrier a sharp drop occurs by dilution of the fissure water with stored pore water. The solutes in the fissure water diffuse into the stored water and in the anaerobic pores of the unsaturated zone microbial denitrification occurs. In the confined aquifer anaerobic conditions prevail and denitrification may occur where the pore dimensions of the Chalk are large enough to accommodate the bacteria.

The N_2 concentration rises with a peak N_2/Ar ratio of 52.02, and is further evidence that denitrification has taken place. The intermediate product of the reaction, NO_2^-, does not appear until after the N_2 peak due to its slower diffusion from the pore water back into the fissure water. With increasing depth the NH_4^+ content rises to a peak of $1.09 mgl^{-1}$ and coincides with the maximum Cl^- concentration. The NH_4^+ is mainly derived from reduced NO_3^- from recharge, which has accumulated over the past 10,000 years since the permafrost meltwater at the end of the Devensian glaciation. The recharge temperatures, together with the ^4He content indicate a mixing process between the stored meltwater in the pores and recent recharge in the fissures. In the unconfined aquifer equilibrium has been reached between the recharge and stored pore water compositions, but with depth in the confined zone this dynamic process is still continuing.

The distribution of the various nitrogen species and the chemical and hydrogeological processes operating in the Berkshire Chalk are summarised in a diagram of the aquifer (figure 5.21).

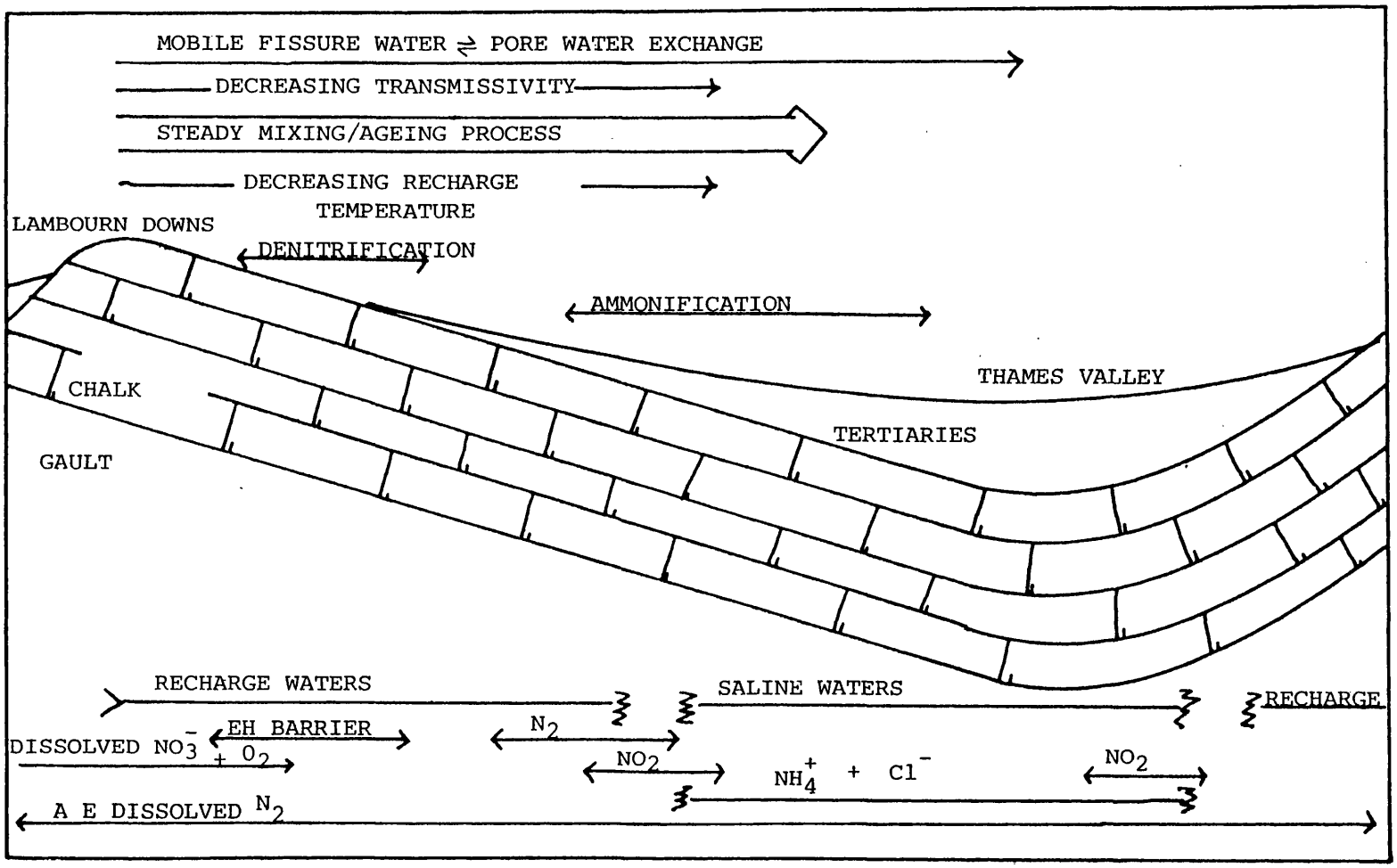


FIGURE 5.21 A SCHEMATIC SECTION OF THE BERKSHIRE CHALK AND UPPER LONDON BASIN, SHOWING THE DOMINANT ZONES OF NITROGEN SPECIES AND THE AREAS IN WHICH THE TRANSFORMATION PROCESSES OPERATE

6. A MODEL OF NITROGEN HYDROGEOCHEMISTRY IN GROUNDWATERS

6.1 INTRODUCTION

The pathways and oxidation-reduction reactions of nitrogen species through the biosphere, lithosphere and atmosphere are interpreted as a cycle. Nitrogen in groundwater is mobile and the conversion processes are relatively rapid until as NH_4^+ it is absorbed on the clay surfaces and fixed. The hydrogeochemistry of nitrogen can, therefore, be regarded as an open ended system, and a sink for the total nitrogen cycle. A mechanistic approach is used to describe the processes involved and a dynamic model is preferred to a budget model, since the case study data are more suited to the modelling of rates and feed-back reactions.

The nitrogen cycle of the soil has been extensively modelled[245]. In rivers and lakes, study has been concentrated on the nitrate levels since these indicate pollution by fertilizers and may lead to the eutrophication of the waters[120,126]. Nitrate levels in rivers respond more rapidly to changes in agricultural practices and thus monitoring of rivers may give analagous information to NO_3^- trends in aquifers[247]. Like rivers, the threat of NO_3^- pollution to aquifers has prompted the study of nitrogen chemistry in the unsaturated[125] and saturated zones[4]. The hydrogeochemistry of nitrogen and its species throughout an aquifer is still incompletely understood.

6.2 A MODEL FOR NO_3^-, N_2, NH_4^+ EQUILIBRIUM IN AQUIFERS WITH INTERSTITIAL STORAGE

A mechanism is proposed whereby the state of the nitrogen chemistry is controlled by the oxidation-reduction environment. Input from the soil zone is mainly in the form of dissolved molecular nitrogen and nitrates. As

the groundwater moves through aquifers in which both interstitial and fracture storage exist, ionic exchange of dissolved species between the mobile fissure water and the static pore fluids occurs by molecular diffusion. Denitrification occurs within the pore spaces, mediated by microorganisms. Continued exchange and increasingly reducing conditions downdip in the aquifer determine the stability of different nitrogen species in the groundwaters. In the most reducing groundwaters, NH_4^+ is formed and is fixed by absorption on clay surfaces.

6.2.1 INPUTS TO THE MODEL

The major inputs of nitrogen in groundwater are dissolved N_2, N_2O and NO_3^- derived from the soil processes. The gaseous nitrogen species in the soil air differ in partial pressure from the atmosphere due to respiration producing increased levels of CO_2 and H_2O (g), and denitrification producing N_2. Thus the N_2/Ar ratio at the base of the soil zone may be either enhanced or reduced compared with the atmospheric equilibrium value. The degree of enhancement is dependent on the soil biotic activity. Ionic species of nitrogen are derived from meteoric sources and from the mineralization and nitrification processes of the soil itself. NO_3^- ($0.3 - 2.5 mgl^{-1}$)[17] and NH_4^+ ($0.1 - 0.2 mgl^{-1}$)[18] from precipitation, though not a significant source of these species, adds to the total soil content. The soil acts as a natural buffer of nitrogen inputs to groundwater, with NH_4^+ being absorbed on clay surfaces and by NO_3^- being denitrified. When excessive amounts of nitrogen fertilizers are applied to the land, or when the soil moisture is too low, the denitrification process does not effectively control the soluble nitrate levels and the nitrate is leached into the unsaturated zone.

Under undisturbed grassland $5 mgl^{-1}$ NO_3^- is typical of the groundwater chemistry, but under fertilized grassland and arable land the concentrations

rise to 10-20mgl^{-1} and 10-50mgl^{-1} respectively. In recent years, the number of high (>11.3mgl^{-1} NO_3.N, WHO limit) NO_3^- level waters has increased, especially in intensive agricultural areas. However, where the land has been cultivated for a long period, the NO_3^- levels appear to have reached an equilibrium value[224], of between 8 and 15mgl^{-1}. The generally high NO_3^- levels in the Lincolnshire Limestone groundwaters have been shown to derive from the soil but localized NO_3^- pollution may also result from silage and sewage spills[5]. The provenance of the nitrate can be determined by its $^{15}N/^{14}N$ isotopic ratio, and as the model is developed the differentiation of mixed sources of NO_3^- will be shown.

6.2.2 MOVEMENT OF NITROGEN SPECIES IN THE UNSATURATED ZONE

The movement of nitrogen species in the groundwater through the unsaturated zone has been well monitored in the Chalk of the UK[4,122,248-250]. This very fine grained pure white limestone provides an almost isotopic homogenous porous medium in which to study the movement of water and solutes in rocks. Groundwater flows through the Chalk, both by rapid recharge through fissures at a flow rate of 2-10m/day[237] and by intergranular flow at a rate of 1m/year. The typical permeability and porosity are 1 x 10^{-3} m/d and 0.35[4]. Tritium studies and incidents of bacterial contamination of the aquifer have provided evidence for these mechanisms of movement[251].

Water moving by fissure flow exchanges ionic species with static pore waters by molecular diffusion[12,18]. Water moves down the profile 20 to 40 times faster than the associated ions[4], and NO_3^- and Cl^- are thought to move more rapidly than Na^+, K^+, and SO_4^{2-} [248]. This slow downward ionic separation has been likened to a chromatographic column[113]. This enables the maintenance of individual seasonal NO_3^- peaks; vertical mixing is very slow.

Profiles of the Chalk show that NO_3^- decreases regularly with depth[248,250]. Movement of water in aquifers such as the Lincolnshire Limestone is more heterogeneous due to frequent impermeable beds[224]. The profile of NO_3^- movement is not well defined but similar modes of fissure and intergranular flow together with pore water exchange occur within these sediments.

No denitrification below the soil zone has previously been assumed[4], but it has also been reported that slight microbial denitrification occurs in the upper few metres of rock[224]. On the basis of the Lincolnshire Limestone and Berkshire Chalk studies, it is shown here that denitrification occurs within the aquifers. This complicates the simple physical separation and dilution processes, and the dynamics of NO_3^- movement are reappraised in the discussion below (Section 6.2.4).

6.2.3 NITRATE REDUCTION

6.2.3.1 Oxidation - Reduction Processes

The redox equilibria have been described for nitrogenous species in natural waters[44] and soils[253]. Nitrogen can exist in five valency states, but for most of the aqueous Eh range N_2 gas is the most stable species. NO_3^- leached to the groundwater is in a metastable state, since it results from the inefficient biological systems of the soil. It is most stable in an oxidized environment of Eh + 699mV, at pH7, but in the aquifers investigated these conditions have not been found, and NO_3^- is rapidly reduced to the stable N_2 gas state. In the reduced aquifer below Eh + 100mV, NH_4^+ is the stable form.

Between Eh + 200mV and + 300mV, although N_2 is the stable form it is possible for any of the nitrogen species to exist at some concentration depen-

dent upon its stability. It is just this range which naturally occurs in the oxidized sections of the aquifers studied and therefore it is possible for a continuous flux of nitrogen species to exist. Localized lenses of reduced ferrous iron occur in the outcrop area of the Lincolnshire Limestone[47], indicating that micro redox systems, with exchange between the different nitrogen valency states, occur in the oxidized zone. These transformation reactions yield energy which can be utilized by microbial organisms as discussed below, and thus the nitrogen chemistry of the oxidized zone is a complex interaction between the redox chemistry and microbiological activity.

6.2.3.2 Microbiological Control of NO_3^- Reduction

Reduction of NO_3^- occurs by two microbially mediated processes[255]. The first is assimilation, where NO_3^- is converted into cell material and fixed as organic nitrogen. The second is dissimilation or respiration and is an oxidative process, for the organisms use the NO_3^- as a terminal hydrogen acceptor instead of oxygen. The end product of the reaction may be NO_2^-, NH_4^+, N_2O or N_2. The process is known as denitrification if molecular nitrogen is produced.

Denitrification requires anaerobic conditions, since the presence of O_2 prevents the formation of NO_3^- reducing enzymes. The process also needs the normal complement of major nutrients and trace elements including Mo, which is necessary for enzyme formation. A carbon source sufficient to support bacterial activity is another prerequisite. In the Chalk carbohydrates have been detected with mannose being the principal component.

The assimilation process reduces NO_3^- under aerobic conditions. In the Lincolnshire Limestone and Berkshire Chalk there was a coincident decline of O_2 and NO_3^- before the rise in the N_2/Ar ratios. Therefore, in the unsaturated zone the NO_3^- is initially reduced by the assimilation process

without the production of N_2. The N_2/Ar ratio started to rise in marginally aerobic conditions and it is possible that microzones of denitrification[256] develop in the intergranular pore spaces, larger than 0.2μm. Thus once the oxygen is removed dissimilation is favoured, and under anaerobic conditions it becomes the dominant process and the end product is N_2.

The rate of nitrate reduction by assimilation is much slower than by dissimilation, since more oxygen is required for respiration than nitrogen is required for cell synthesis. Data concerning the rate of reduction are scarce but for Micrococcus denitrificans, nitrogen gas was produced from NO_3^- under anaerobic conditions at 59μg (0.002mM) and 56μg (0.002mM)[258] per mg of dry cell per hour.

In the Lincolnshire Limestone the presence of anaerobic denitrifying bacteria at Lenton and the occurrence of $0.101 mgl^{-1}$ NO_2^- confirm that dissimilation of nitrate takes place in the anaerobic aquifer. The increase in the proportion of anaerobes in the bacteria population continues downdip, but the nitrogen gas concentration is reduced beyond the Eh barrier. It is probable that in the deep aquifer the end product of denitrification is NH_4^+.

6.2.4 DISSOLVED MOLECULAR NITROGEN

In groundwater dissolved molecular nitrogen is derived from three sources: air dissolved during equilibration of the infiltrating water with the atmosphere in the soil zone, variable concentrations of air incorporated through total solution of air bubbles trapped during infiltration, and nitrogen derived from denitrification. These various components of the total dissolved nitrogen concentration can be delimited using solubility data and isotopic evidence. Some assumptions must be made to estimate the various nitrogen sources in a groundwater. There must be only one process of nitrate reduction

which has a constant isotopic fractionation effect. Chain reactions and the recycling of nitrogen as previously discussed are inherent in natural systems, so that nitrogen isotope values are the result of a combination of processes, and at best can be used as empirical indicators of the evolution of nitrogen.

The concentration of air equilibrated dissolved nitrogen is controlled by its solubility and varies with temperature. In the soil zone the partial pressure of nitrogen is enhanced to as much as 0.9 atmosphere due to NO_3^- reduction. From figure 6.1, the initial N_2/Ar ratio at recharge can be calculated, since the recharge temperature can be estimated from the inert gas content, and thus the initial nitrogen concentrations $[N_2]_T$ is found. If the composition of the soil atmosphere is known an adjustment can be made at this stage. Where excess air is suspected a correction may be applied[138].

Once the initial recharge N_2 concentration has been established, then the contribution from the denitrification process can be calculated from the equation:

$$[N_2/Ar] = \frac{[N_2]_T + [N_2]_D}{[Ar]_T}$$

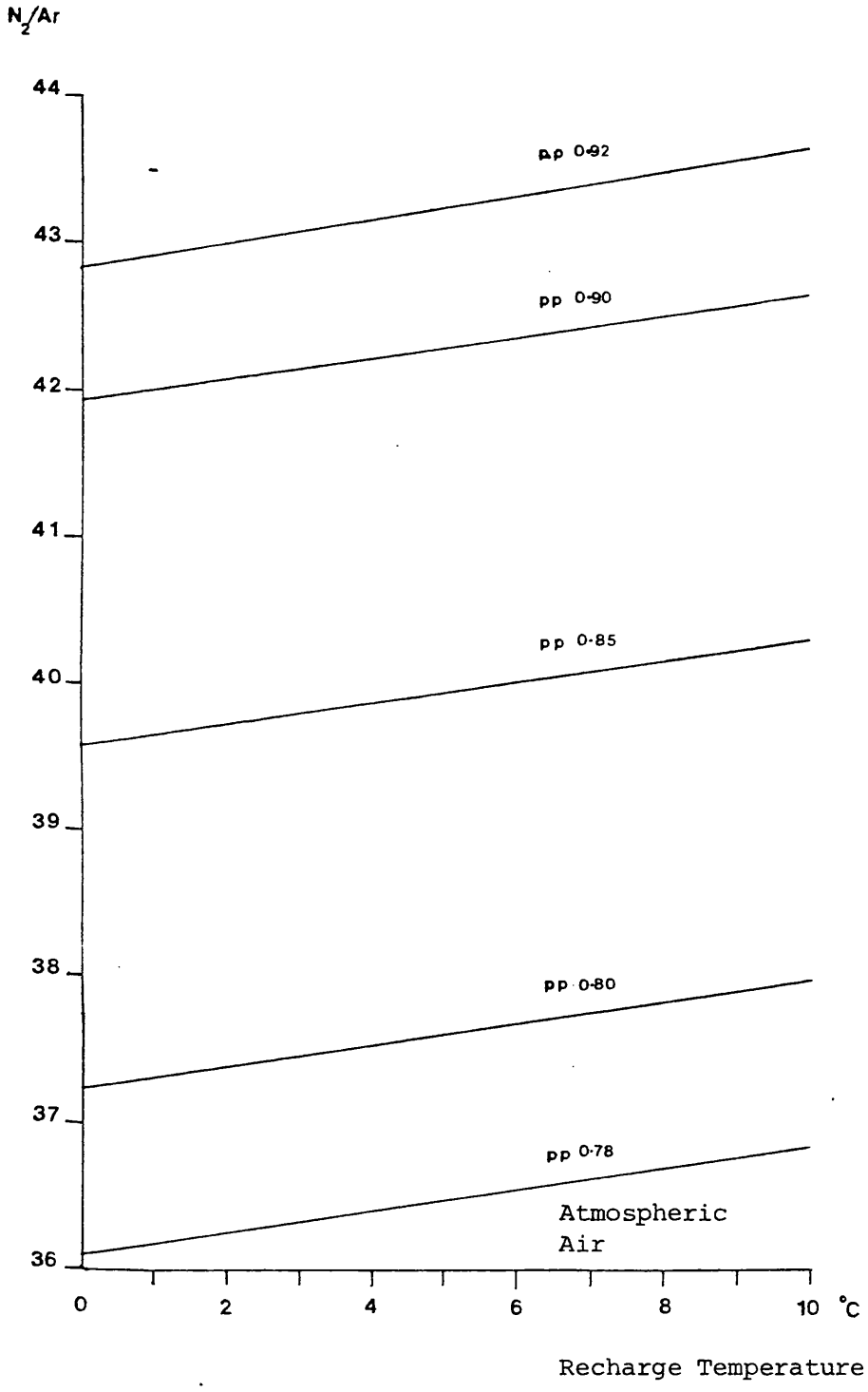
where $[N_2/Ar]$ = N_2/Ar ratio of groundwater

$[N_2]_D$ = concentration of dissolved nitrogen derived from denitrified NO_3^-

$[N_2]_T$ = concentration of dissolved nitrogen equilibrated with soil atmosphere at recharge temperature, T

$[Ar]_T$ = concentration of dissolved argon equilibrated with soil atmosphere at recharge temperature, T.

This is shown graphically in figure 6.2 and the amount of nitrogen $[N_2]_D$ derived from denitrification can be estimated from the observed N_2/Ar ratio. This can be related to the observed NO_3^- input concentration at recharge



p.p. = partial pressure N_2

FIGURE 6.1 THE N_2/Ar RATIO FOR GROUNDWATERS RECHARGED AT TEMPERATURES FROM 0-10°C AND AT PARTIAL PRESSURES OF SOIL NITROGEN ENHANCED ABOVE ATMOSPHERIC AIR

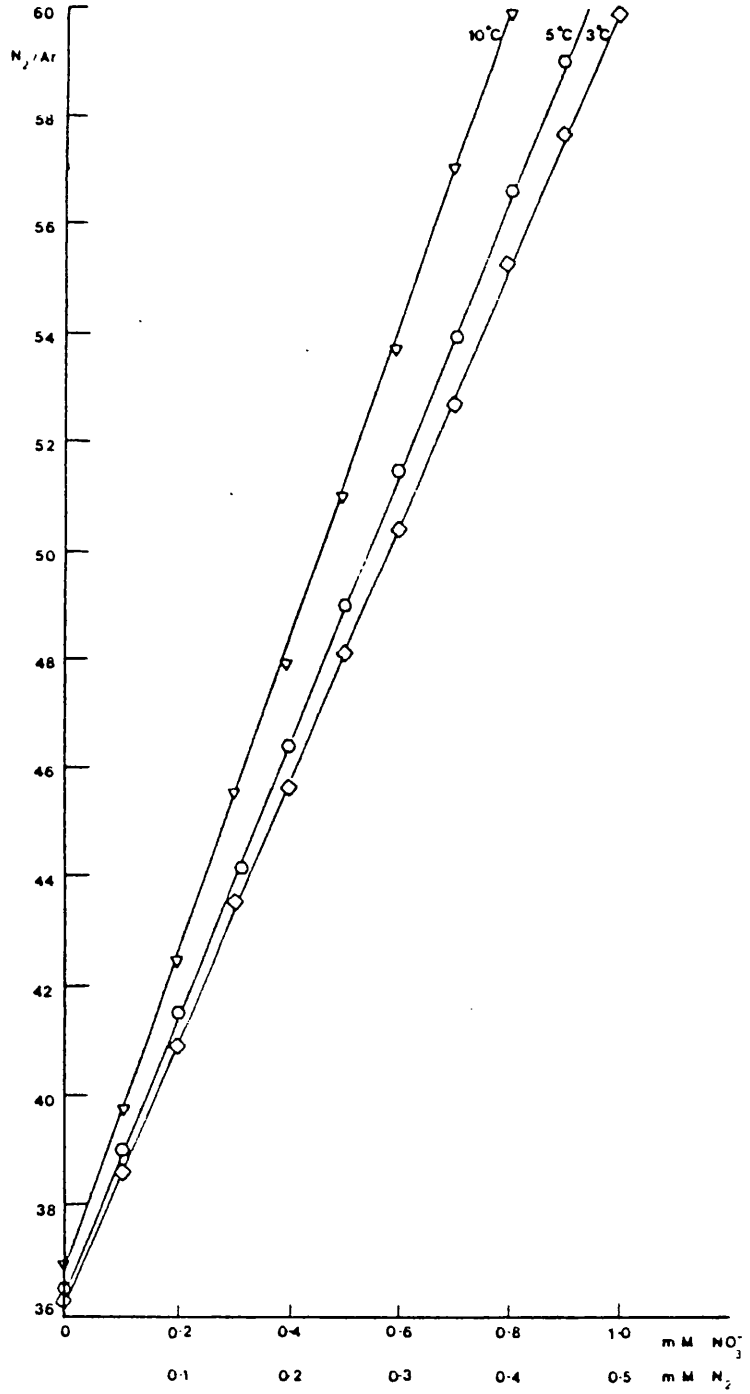


FIGURE 6.2 THE ENHANCEMENT OF THE DISSOLVED N_2/Ar RATIO IN GROUNDWATERS RESULTING FROM NO_3^- DENITRIFICATION AT VARIOUS RECHARGE TEMPERATURES

$[NO_3^-]_R$ to find the fraction of nitrate denitrified.

$$F = \frac{[N_2]_D}{[NO_3^-]_R} = \frac{[NO_3^-]_R - [NO_3^-]_S}{[NO_3^-]_R}$$

where F = the fraction denitrified

$[NO_3^-]_S$ = the concentration of NO_3^- in the groundwater at a specific site.

Dissolved nitrogen in equilibrium with the atmosphere has a $\delta^{15}N$ value of +0.7°/oo[53], $[\delta^{15}N]_A$. Using this, the $\delta^{15}N$ content of the N_2 derived from denitrification of NO_3^- can be calculated and the predicted $\delta^{15}N$ of the proportionately mixed $[N_2]_T$ and $[N_2]_D$ compared with the observed $\delta^{15}N$ of total dissolved nitrogen, $[\delta^{15}N_2]$. The $\delta^{15}N$ of $[N_2]_D$ is calculated where a fractionation factor

$$\alpha = \frac{K_1}{K_2} \equiv \text{ratio of reaction rates } K_1 \text{ and } K_2 \text{ between each isotope species}$$

and an enrichment factor ε are assumed for dentrification where,

$$\varepsilon = (\alpha - 1) \times 1000.$$

In this model, ε is taken as -30 ± 6°/oo, the value derived for the denitrification process in the Auob sandstone aquifer, South Africa[28]. There, due to the semi arid climate of the recharge area nitrate reduction did not commence until after the onset of anaerobic conditions, and so only one process that of dissimilation occurred.

The fractionation process is analagous to a Rayleigh distillation, and the relative isotope ratios of dissolved nitrogen derived from nitrates of various isotopic values can be calculated from:

$$\left[\frac{[\delta^{15}N_2]_D}{1000}\right] = \left[\frac{[\delta^{15}NO_3^-]_R}{1000} + 1\right]\left[\frac{1-(1-F)^{\alpha}}{F} - 1\right]$$

where $[\delta^{15}N_2]_D$ = the isotopic composition of nitrogen derived from nitrate

$[\delta^{15}NO_3^-]_R$ = the recharge isotopic composition of the nitrates

F = the fractionation of NO_3^- denitrified

α = as defined above.

This is shown graphically in figure 6.3.

The $\delta^{15}N$ value for a nitrogen gas mixture $[\delta^{15}N_2]_M$, denitrified and dissolved N_2, is given by:

$$[\delta^{15}N_2]_M = ([\delta^{15}N_2]_A \times F_A) + ([\delta^{15}N_2]_D \times F_D)$$

where F_A = the fraction of gas derived from the atmosphere

F_D = the fraction of gas derived from denitrification.

and is shown in figure 6.4.

Comparison of the calculated and actual $\delta^{15}N$ values of the dissolved nitrogen can be made. If the values are in agreement, then the groundwater nitrogen is derived in the specified recharge environment. If the values do not agree then a process of optimization of the recharge variables (temperature, soil atmosphere composition and the denitrification fractionation factor) is carried out. A flow diagram for the process is given in figure 6.5.

It is possible to define the origin of dissolved nitrogen and to predict the rate of denitrification with the above method for a simple hydrogeochemical situation, where recharge is rapid and denitrification occurs within the saturated zone. However, in the aquifers studied the nitrogen

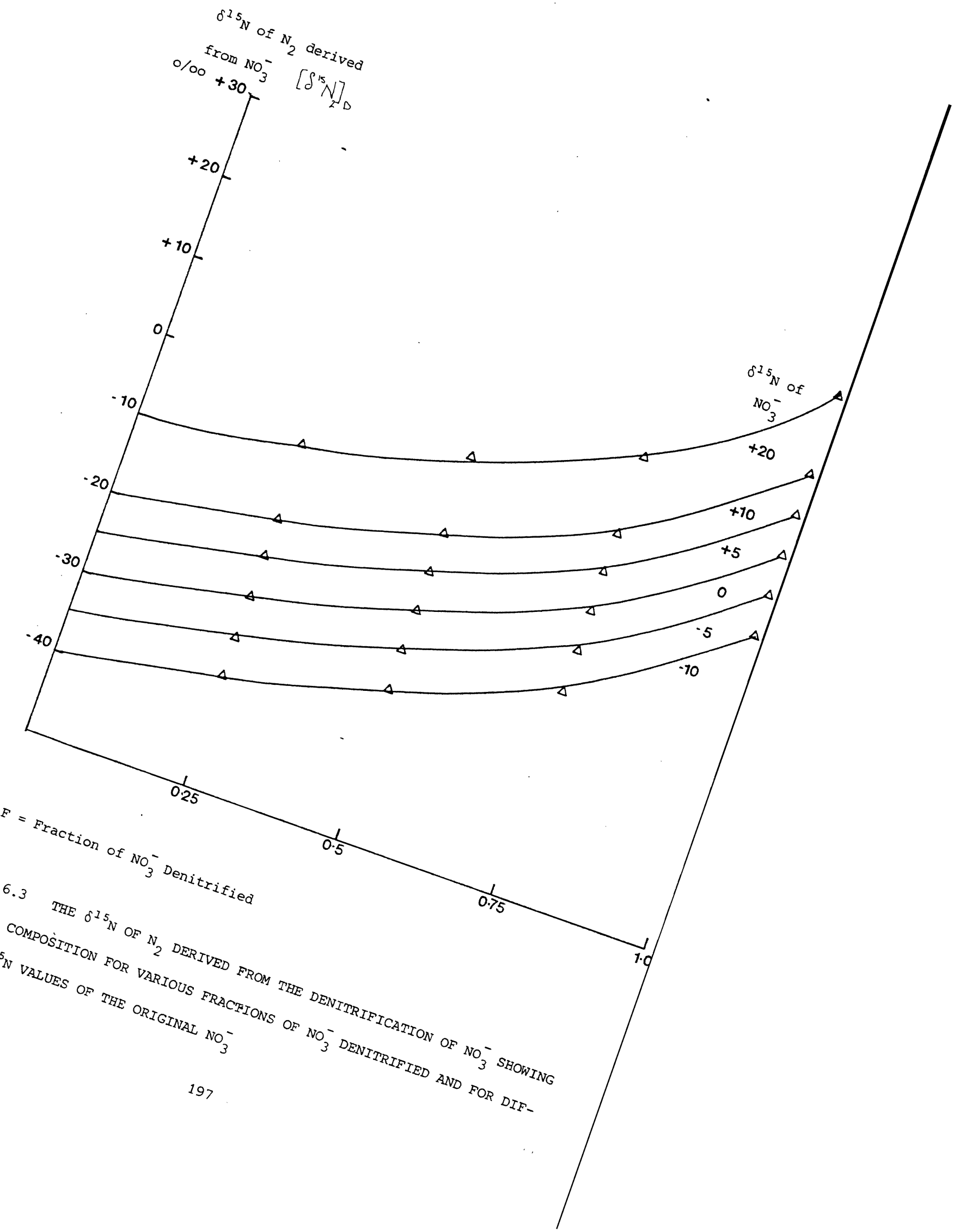
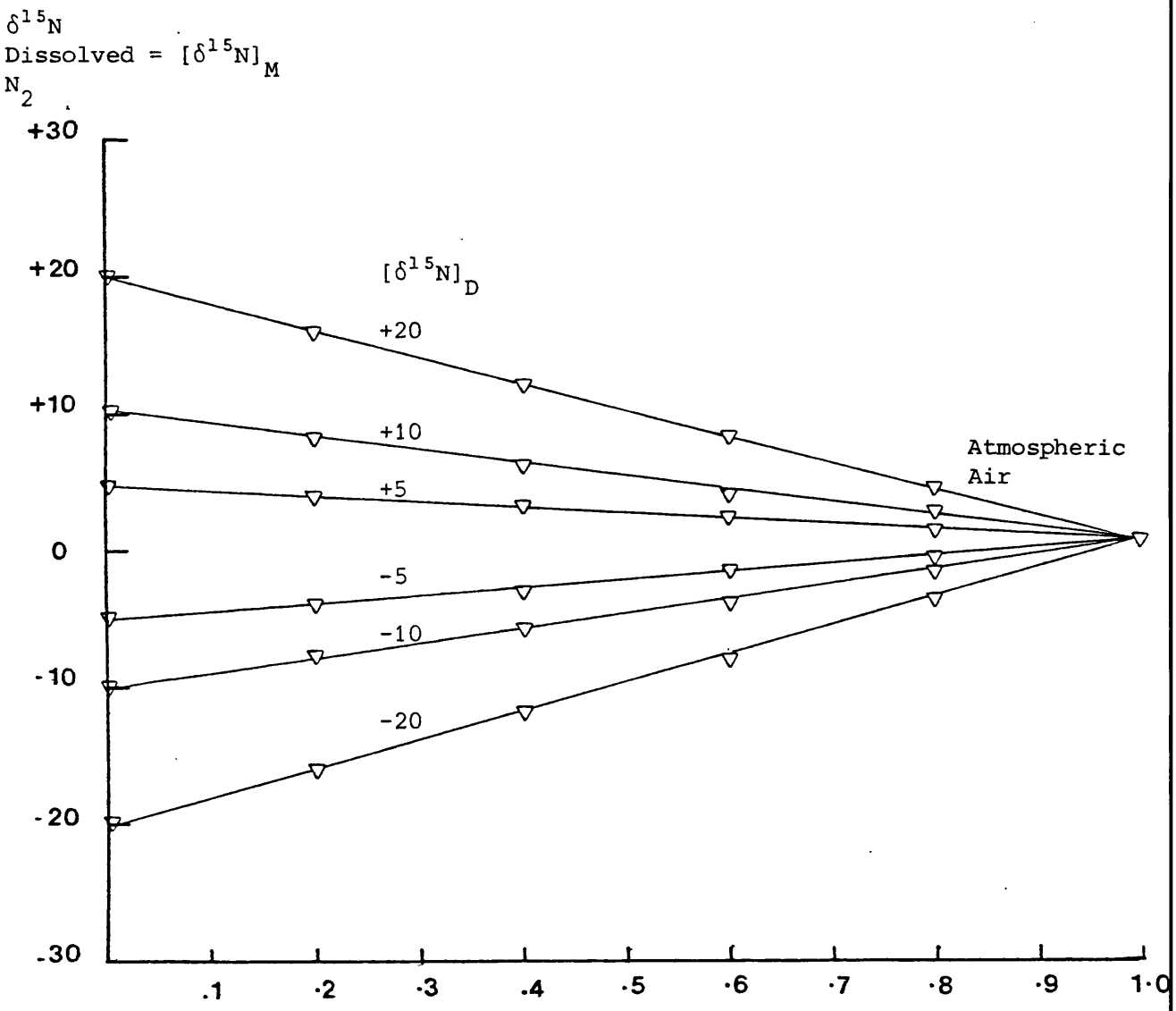
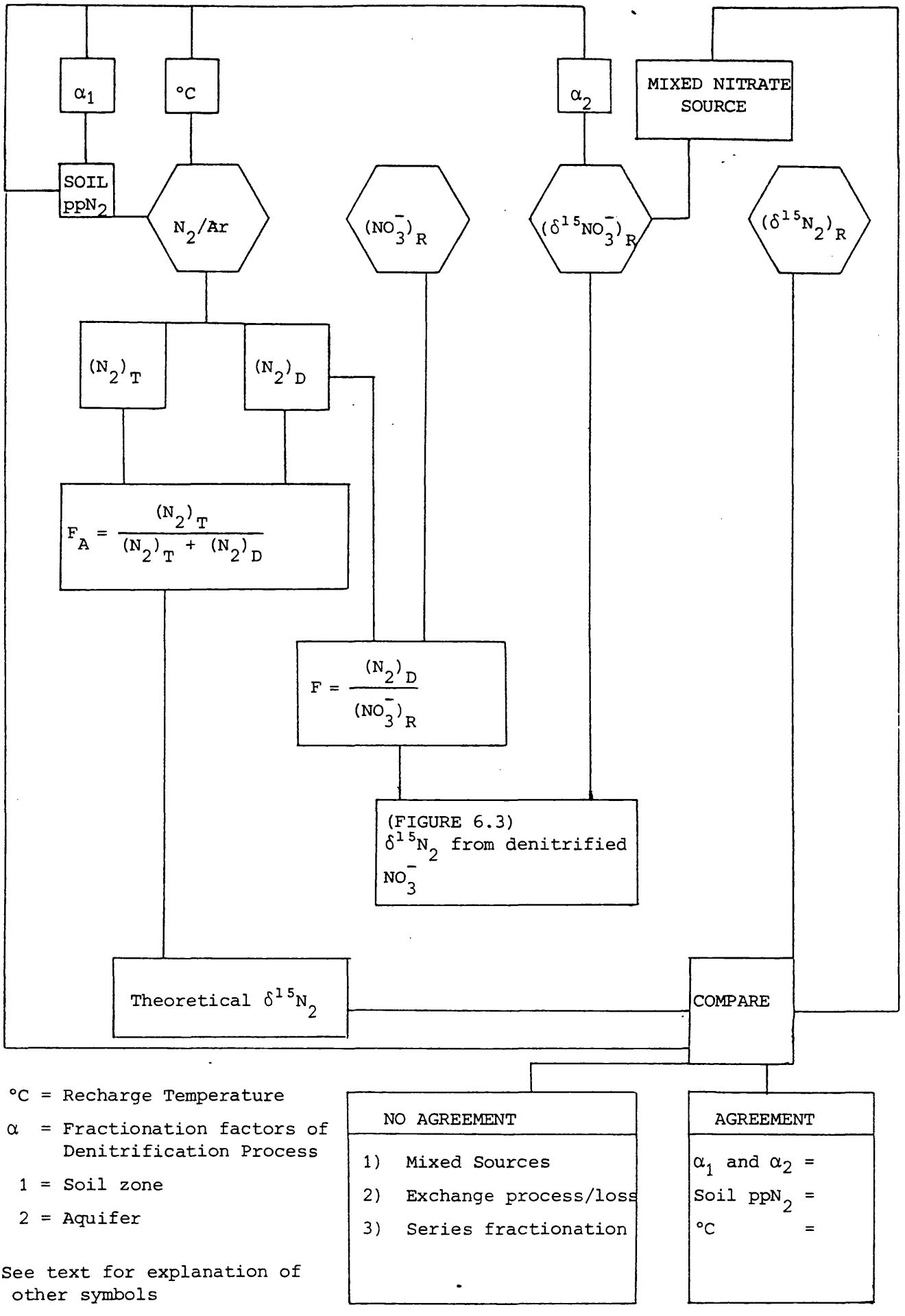


FIGURE 6.3 THE $\delta^{15}N$ OF N_2 DERIVED FROM THE DENITRIFICATION OF NO_3^- SHOWING THE $\delta^{15}N$ COMPOSITION FOR VARIOUS FRACTIONS OF NO_3^- DENITRIFIED AND FOR DIFFERENT $\delta^{15}N$ VALUES OF THE ORIGINAL NO_3^-



F_A = Fraction of N_2 gas derived from atmosphere

FIGURE 6.4 THE $\delta^{15}N$ VALUE FOR A NITROGEN GAS MIXTURE $[\delta^{15}N_2]_M$ DERIVED FROM DENITRIFIED NO_3^-, $[\delta^{15}N_2]_D$, AND DISSOLVED FROM THE ATMOSPHERE, $[\delta^{15}N_2]_A$



°C = Recharge Temperature

α = Fractionation factors of Denitrification Process

1 = Soil zone

2 = Aquifer

See text for explanation of other symbols

FIGURE 6.5 MODEL OF $\delta^{15}N_2$ IN GROUNDWATER

hydrogeochemistry is more complex, for denitrification occurs at three horizons in the aquifer (figure 6.6). Initially, denitrification takes place in the soil horizon. This results in an increase in the partial pressure of nitrogen in the soil atmosphere and due to fractionation a lighter $^{15}N/^{14}N$ composition. NO_3^- remaining in the soil and then leached to the unsaturated zone consequently has a more positive $\delta^{15}N$ value. Denitrification may occur in this zone in the saturated anaerobic pore spaces mediated by a microbial population which differs in species composition from the soil. It is probable that the fractionation factor also differs. In the saturated zone, denitrification will continue in yet another chemical and microbiological environment. Thus it is possible for nitrogen derived from the denitrification of nitrates to have three different sources and isotopic compositions. By using complete nitrogen hydrogeochemical and isotope analyses with the above method (figure 6.6) for each zone of the aquifer, their relative importance in the denitrification process can be assessed.

The rate of evolution of dissolved nitrogen derived from denitrification has been estimated to commence 13000 years after recharge and to take 14,000 years for completion in the Auob aquifer of South Africa[145]. The slow rate of denitrification may result from the lack of organic nutrients in the soil due to poor soil development and lack of vegetation in the semi-arid climate. In the Lincolnshire Limestone and Berkshire Chalk, the rate of NO_3^- reduction is very rapid with the decline of NO_3^- concentrations occurring a short distance after confinement and in groundwater containing post 1953 tritium. Therefore, the reduction of nitrates at least in the fissure water takes less than 30 years. However, the evolution of molecular nitrogen released after denitrification has occurred in the pore waters is a much slower process. In the Berkshire Chalk denitrification is completed within 10,000 years due to the decline of the observed N_2/Ar related to the recharge temperature and a similar time scale is assumed for the Lincolnshire Limestone. Therefore, since the rate of nitrate reduction in the humid environment of the UK aquifer

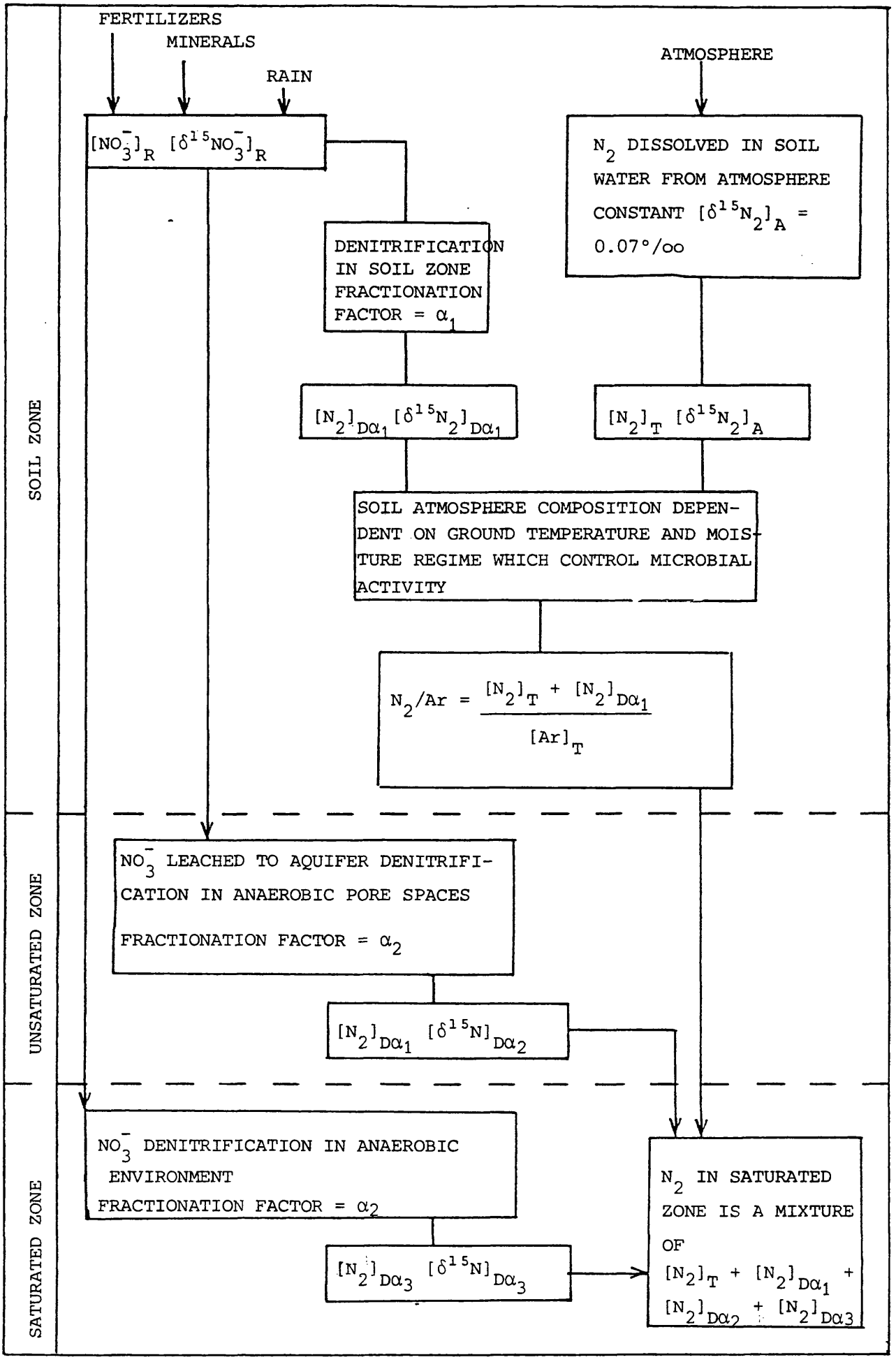


FIGURE 6.6 N_2 DERIVED FROM DENITRIFICATION IN THREE ZONES OF THE RECHARGE PROFILE

is more rapid, the fractionation factor for denitrification is likely to be significantly different from the semi arid land conditions, and must be considered in the optimization process on the model of $\delta^{15}N$ of dissolved nitrogen in groundwater.

The overall trend of a lighter isotopic composition for dissolved nitrogen with depth in the aquifer is a result of the combined effects of chemical reactions and physical diffusion and exchange processes. In the sample from the deepest part of the Lincolnshire Limestone aquifer, the dissolved nitrogen became enriched as the reducing chemical environment favoured the production of ammonium and further fractionations occurred during the ammonification process.

6.2.5 THE TRANSFORMATION OF DISSOLVED NITROGEN TO AMMONIUM

The $N \equiv N$ bond of molecular nitrogen is very stable but at low Eh it can be reduced to NH_4^+. The reaction does not attain equilibrium under natural conditions because N_2 is protected by high activation energies. Biological nitrogen fixation is possible in the aquifer, and occurs in the organelles of bacteria where the redox environment is held very low by leghemoglobin[259], and the enzyme nitrogenase catalyses the convertion of N_2 to NH_4^+. Under anaerobic conditions bacteria can directly transform NO_3^- to NH_4^+ [260]. A small contribution of the NH_4^+ may be derived from the recharge zone through these processes, but the cation is readily assimilated or absorbed on to the surfaces of colloids.

Whether the conversion of N_2 to NH_4^+ at depth in the aquifer is mediated by bacteria is unknown. The chemical environment at depth in both aquifers is conducive to the production of NH_4^+. A general increase in NH_4^+ concentration was observed in both the Lincolnshire Limestone and the Berkshire Chalk. It is not possible to calculate quantitatively the source of the NH_4^+

because it is readily absorbed. Thus this is the end of the groundwater nitrogen reaction succession and in this fixed state the nitrogen molecule can only re-enter the nitrogen cycle by way of geological processes on a geological time scale.

6.2.6 THE EFFECTS OF SOIL AND CROP MANAGEMENT ON NITROGEN HYDROGEOCHEMISTRY

Agricultural practices, including tillage, drainage and the application of fertilizers, modify the physical and chemical state of the soil, to maintain its fertility and thus its productivity. Soil porosity, the most important factor influencing gas and water movement is lowered by cropping due to the associated decline in organic matter content, and the consequent breakdown of granulation. The pore spaces have also been found to decrease in size[14]. Both these changes encourage denitrification due to poor aeration and drainage. Thus the soil atmosphere composition at recharge is dependent on the soil porosity and land use, for the nitrogen partial pressure will probably be higher in a wet clayey soil than in a sand.

The use of inorganic fertilizers has increased very rapidly over the past 40 years from 2% of the total available nitrogen in 1938/1939 to over 25% in 1970/1972. The highest region for fertilizer application rates in the UK is South Lincolnshire with over 80kg N ha^{-1}. Over the Chalk the values vary between 40 and 80kg N ha^{-1} [265]. Locally even higher rates are used with up to 400kg N ha^{-1} on managed grasslands[224]. Uptake by arable crops may account for 40% - 60% of the applied fertilizer, and under grassland the uptake may be as much as 80% - 90% [266]. The recovery of the fertilizer nitrates by plants is dependent on the physical soil condition and determines the proportion available for denitrification and leaching to groundwater.

The effect of fertilizer application on nitrogen hydrochemsitry differs depending on where denitrification occurs. If reduction of NO_3^- occurs within

the soil zone then nitrogen is released increasing the partial pressure of the soil atmosphere. The dissolved N_2/Ar ratio of groundwater equilibrated with this atmosphere will be enhanced. At a fertilizer application rate of 100kg N ha^{-1} the ratio will be raised from 36.8 to 39.5. However, if this fertilizer is leached through the soil zone and is subsequently denitrified within the aquifer then only N_2 is released to increase the N_2/Ar ratio to 74.32 (Appendix D).

Thus where soils are well drained and aerated, as on the Berkshire Chalk, total denitrification does not occur in the soil zone. High N_2/Ar ratios are therefore probable due to denitrification occurring within the aquifer. Where the soils overlying the aquifers are less permeable the effect of pollution by nitrate fertilizers will be reduced by denitrification in the soil horizon. Thus the nitrogen hydrogeochemistry and especially the sensitive N_2/Ar ratio and $^{15}N/^{14}N$ ratios are highly dependent on the soil zone reactions and agricultural practices.

7. CONCLUSIONS

7.1 THE DISTRIBUTION OF NITROGEN SPECIES IN GROUNDWATERS

In the Lincolnshire Limestone and Berkshire Chalk, sequences of nitrogen oxidation-reduction reactions with passage into the aquifer have been demonstrated. In the unsaturated zone and in the shallow confined aquifer, NO_3^- and N_2 were the stable species. At outcrop in the Lincolnshire Limestone, dissolved nitrate exceeded $60mgl^{-1}$ and in the Chalk averaged $21mgl^{-1}$. Just into the confined aquifer the NO_3^- was reduced to NO_2^- and N_2. In both aquifers low NO_2^- concentrations ($<0.4mgl^{-1}$) were found. As the groundwater moved into the reduced part of the aquifer, NO_3^- declined to trace values and further into this zone, the dissolved N_2 reached a peak. In the deep confined aquifers, some reduction of N_2 to NH_4^+ has been shown to occur. The NH_4^+ reached $0.6mgl^{-1}$ in the Lincolnshire groundwaters and $1.1mgl^{-1}$ in the Berkshire groundwaters. This corresponds to the reduction of about 7% of the dissolved N_2.

7.2 DISSOLVED N_2 IN GROUNDWATERS

The dissolved N_2 in groundwaters was monitored by the determination of the N_2/Ar ratio. In this study an analytical method using mass spectrometry was developed with a precision of $2\sigma = 2.32$ and an accuracy of $\pm$ 4.9 ratio units. The accuracy was not sufficient for a quantitative interpretation of the nitrogen hydrogeochemistry, but the results showed semi-quantitative trends.

The dissolved N_2/Ar ratio in groundwaters is dependent on the conditions in the soil horizon of the recharge area. The partial pressure of N_2 in air is 0.78, but this may be increased in soil air due to nitrate reduction. Denitrification of nitrate fertilizer which was applied at the rate of

100kg N ha^{-1} would increase the partial pressure to 0.796 (Appendix D). The initial N_2/Ar ratio in the groundwater leaving the soil zone would therefore be between 36.8 and 39.5, provided that there was no entrainment of soil air. A large proportion of applied N fertilizer moves through the soil zone without reduction and denitrification of this nitrate in the confined aquifer can cause the N_2/Ar ratio in the groundwater to be increased to 74.3. Evidence of this increase has been found both in the groundwater from the Lincolnshire Limestone and the Berkshire Chalk. The N_2/Ar ratios increased as nitrate reduction proceeded to approximately 63 in the Lincolnshire Limestone and to approximately 52 in the Berkshire Chalk. Further into the confined part of the aquifer these ratios decreased due to the reduction of dissolved N_2 to NH_4^+. This is supported by the presence of NH_4^+ in the groundwaters.

7.3 $^{15}N/^{14}N$ RATIO OF DISSOLVED NITROGEN SPECIES

The $^{15}N/^{14}N$ ratios of dissolved nitrogen and nitrogen species were determined for the Lincolnshire Limestone groundwaters. The ratios are expressed as $\delta^{15}N$ values relative to atmospheric N_2 as a standard, and could be determined to within 0.65°/oo. The dissolved nitrate in these groundwaters had $\delta^{15}N$ ranging from +2.8 to +7.7°/oo. In the part of the aquifer where NO_3^- reduction occurs the $\delta^{15}N$ of dissolved N_2 was found to be between -0.73 and +3.56°/oo. This enhancement over the atmospheric N_2 values confirms the presence of dissolved N_2 which has been produced by reduction of the isotopically heavier NO_3^-. The $\delta^{15}N$ value for the dissolved N_2 increases as N_2 is reduced to NH_4^+ in the aquifer. This is the result of isotope fractionation in the reduction reaction, which favours the lighter isotope.

7.4 NITRATE REDUCTION BY PHYSICAL AND BIOCHEMICAL PROCESSES

The groundwater NO_3^- content decreases in the downdip direction in the aquifer. This decrease is due partly to NO^-_3 metabolism by microorganisms

in the aerobic zone and partly the dilution of the fissure water by low nitrate content pore waters. In the unsaturated zone, NO_3^- reduction occurs due to the action of anaerobic bacteria within the pore spaces of the rock. For such reduction to occur, the pore spaces must be large enough to accommodate the nitrate reducing bacteria. This is possible in the Lincolnshire Limestone, but it is not known to what extent it is important in the much smaller pore spaces of the Chalk. In the confined aquifer, anaerobic bacteria can cause NO_3^- reduction in both the fracture and pore fluids, but reduction in the latter is quantitatively much more significant. The reduction products diffuse from the pores into the fractures, and the gaseous N_2 probably diffuses out of the pores more rapidly than NO_2^-. This causes the N_2/Ar to increase in the downdip direction before an increase in the NO_2^- content is observed.

In the Lincolnshire Limestone groundwaters three denitrifying bacteria were identified: Chromobacterium violateum, Pseudomonas indinium and Bacillus cereus v. mycoides. These species of bacteria are typical of soils.

7.5 INERT GASES AS INDICATORS OF RECHARGE TEMPERATURE AND GROUNDWATER MIXING PROCESSES

The inert gas contents of the Berkshire Chalk groundwaters were used to calculate their recharge temperatures, and showed a linear trend from 10°C close to outcrop to 1.4°C in the deep aquifer. The oldest waters in the Berkshire Chalk have a ^{14}C age of 10,000 years and the low recharge temperature suggests they were derived from permafrost meltwater. The recharge temperatures, ^4He and NH_4^+ contents all increase directly with the Cl^- concentration and this suggests that this is a groundwater ageing trend. This may be explained as a progressive mixing process between the stored in the pores and recent recharge waters in the fissures. In the unconfined aquifer the pore waters have been replaced subsequent to the last cold phase

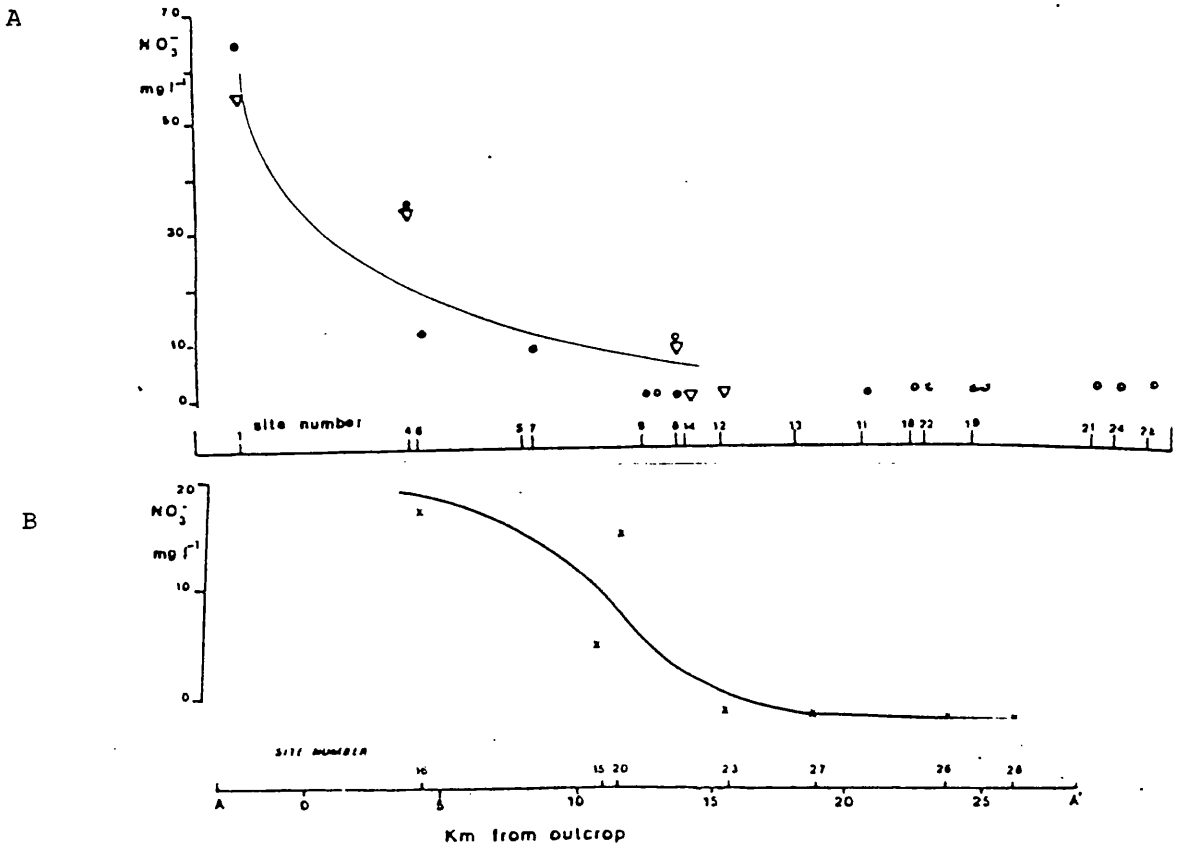
but at depth in the confined zone, the pore waters are considered to be melt-waters from the Devensian glaciation.

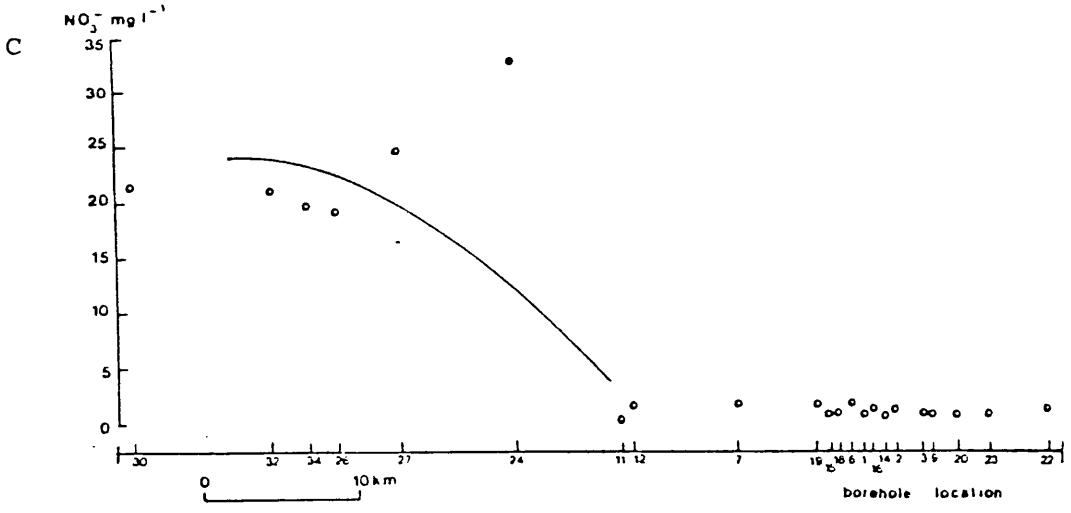
7.6 THE RATE OF NITRATE DIMINUTION AND THE EFFECT OF AGRICULTURAL PRACTICES ON NITROGEN HYDROGEOCHEMISTRY

The agricultural practices of tillage, drainage and fertilizer application have reduced the denitrifying capacity of the soil and increased the nitrogen input to groundwaters. Nitrate leached to the unsaturated zone is lowered in concentration by two processes . Dilution of fissure water NO_3^- by stored pore water is the most important process, but where NO_3^- accumulates in the pore waters the effectiveness of such dilution is lessened. The second process, that of denitrification occurs subsequently, both within the saturated pores of the unsaturated zone and a short distance after confinement in the saturated zone. Both the presence of NO_2^- and enhanced N_2 levels are evidence for this. The nitrate concentrations are lowered to trace levels in groundwaters containing post 1953 tritium, suggesting that the dilution process is relatively rapid. The rate of diffusion of the products of denitrification from the pore water back to the fissure water masks the actual rate of NO_3^- reduction but this process is completed in the Berkshire Chalk within 10000 years.

In the Lincolnshire Limestone, along the southern Section, the overall rate of decrease of nitrate levels is $4.1 mgl^{-1}$ NO_3^- km^{-1}. Along the northern Section the NO_3^- diminution rate is lower at $1.6 mgl^{-1}$ NO_3^- km^{-1}. This decline reflects the dilution process since N_2 from denitrification is not evolved until NO_3^- levels of $10 mgl^{-1}$ occur. The shape of the plotted NO_3^- values (figure 7.1) shows a more sigmoidal curve for the northern Section indicating the incursion of higher NO_3^- values further into the aquifer. In the Berkshire Chalk groundwaters this effect is even more pronounced, where the rate of

nitrate diminution is lowered to 0.66mgl^{-1} NO_3^- km^{-1} (figure 7.1). Thus where the gradient of the down dip NO_3^- concentration profile is steep the processes of dilution by pore waters and denitrification have the capacity to lower the NO_3^- inputs and maintain a stable NO_3^- concentration profile. However, where the NO_3^- concentrations are not immediately reduced, this indicates that the pore waters are becoming polluted by NO_3^- and that the dilution process is no longer effective. This results in the migration of the NO_3^- concentration profile down dip. Therefore, since the rate of decrease of NO_3^- levels is lowest in the Chalk and the shape of the NO_3^- concentration profile indicates contaminated pore waters, the threat of NO_3^- pollution to the Berkshire Chalk groundwater supplies is most acute.





A Southern Lincolnshire Limestone section
Nitrate Diminution Rate = 4.1mgl^{-1} NO_3^- km^{-1}

B Northern Lincolnshire Limestone Section
Nitrate Diminution Rate = 1.6mgl^{-1} NO_3^- km^{-1}

C Berkshire Chalk Nitrate Diminution Rate = 0.66mgl^{-1} NO_3^- km^{-1}

FIGURE 7.1 THE RATE OF NITRATE DIMINUTION IN THE LINCOLNSHIRE LIMESTONE AND THE BERKSHIRE CHALK, SHOWING THE CHANGE IN SHAPE OF THE NITRATE CONCENTRATION CURVE AS THE RATE OF DIMINUTION DECREASES AND DILUTION BY PORE WATERS BECOMES LESS EFFECTIVE

7.7 SUGGESTIONS FOR FURTHER WORK

The relationship and rate of movement between the soil horizon and the unsaturated zone needs to be studied in detail. This could be achieved by analysis of a cored borehole to produce profiles of the nitrogen species and their isotope ratios and tritium profiles, both in fissure and pore waters. A better correlation with an age dating technique, such as tritium, would aid in the determination of the rate of denitrification. Monitoring the change in shape of the nitrate profile from outcrop to the oxidation-reduction zone interface would determine the extent of pore water contamination and the decreased effect of the dilution process.

The work on groundwater microbial populations could be extended by more detailed surveys and comparisons made between the soil and the aquifer. The fractionation factors for bacteria identified as mediating the denitrification process need to be determined so that a quantitative kinetic approach can be adopted.

Closer study of the behaviour of NH_4^+ in the deep aquifer is required. It is not known whether the reaction of N_2 to NH_4^+ is a physical or a biologically mediated process. At the low concentrations of NH_4^+ the determination of the $^{15}N/^{14}N$ ratio is difficult but this could clarify the reaction mechanism.

All N inputs to the groundwater should ideally be identified and measured for $^{15}N/^{14}N$ ratios and added to the basic $\delta^{15}N_2$ model. Once all the inputs and reactions are determined or predicted, a computer optimization process could be carried out and used to predict the outcome of particular hydrological events or incidents of pollution on the nitrogen hydrogeochemistry.

APPENDIX A

gas solubility -10 to 80 deg cent
data from Benson and Krause 1972 [41]

t °C	Ar cm^3/cm^3 water	N2 cm^3/cm^3 water	N2/Ar
-10	6.96122 E-4	2.44818 E-2	35.1688
-9.9	6.93754 E-4	2.44054 E-2	35.1787
-9.8	6.91399 E-4	2.43294 E-2	35.1886
-9.7	6.89057 E-4	2.42537 E-2	35.1984
-9.60001	6.86727 E-4	2.41785 E-2	35.2083
-9.50001	6.8441 E-4	2.41036 E-2	35.2181
-9.40001	6.82106 E-4	2.40291 E-2	35.2279
-9.30001	6.79814 E-4	0.023955	35.2377
-9.20001	6.77534 E-4	2.38813 E-2	35.2474
-9.10001	6.75267 E-4	0.023808	35.2572
-9.00002	6.73012 E-4	0.023735	35.2669
-8.90002	6.70769 E-4	2.36624 E-2	35.2766
-8.80002	6.68538 E-4	2.35902 E-2	35.2863
-8.70002	6.66319 E-4	2.35184 E-2	35.296
-8.60002	6.64112 E-4	2.34469 E-2	35.3056
-8.50002	6.61917 E-4	2.33758 E-2	35.3153
-8.40002	6.59733 E-4	0.023305	35.3249
-8.30003	6.57561 E-4	2.32346 E-2	35.3345
-8.20003	6.55401 E-4	2.31646 E-2	35.3441
-8.10003	6.53252 E-4	2.30949 E-2	35.3537
-8.00003	6.51114 E-4	2.30255 E-2	35.3632
-7.90003	6.48988 E-4	2.29565 E-2	35.3728
-7.80003	6.46874 E-4	2.28879 E-2	35.3823
-7.70004	6.4477 E-4	2.28196 E-2	35.3918
-7.60004	6.42678 E-4	2.27516 E-2	35.4013
-7.50004	6.40596 E-4	0.022684	35.4108
-7.40004	6.38526 E-4	2.26168 E-2	35.4203
-7.30004	6.36466 E-4	2.25498 E-2	35.4297
-7.20004	6.34418 E-4	2.24832 E-2	35.4391
-7.10004	6.3238 E-4	0.022417	35.4486
-7.00005	6.30353 E-4	0.022351	35.458
-6.90005	6.28337 E-4	2.22854 E-2	35.4673
-6.80005	6.26331 E-4	2.22201 E-2	35.4767
-6.70005	6.24335 E-4	2.21552 E-2	35.486
-6.60005	6.2235 E-4	2.20906 E-2	35.4954
-6.50005	6.20376 E-4	2.20262 E-2	35.5047
-6.40005	6.18411 E-4	2.19623 E-2	35.514
-6.30006	6.16457 E-4	2.18986 E-2	35.5233
-6.20006	6.14514 E-4	2.18352 E-2	35.5325
-6.10006	6.1258 E-4	2.17722 E-2	35.5418
-6.00006	6.10656 E-4	2.17094 E-2	35.551
-5.90006	6.08743 E-4	0.021647	35.5602
-5.80006	6.06839 E-4	2.15849 E-2	35.5694
-5.70007	6.04945 E-4	2.15231 E-2	35.5786
-5.60007	6.03061 E-4	2.14616 E-2	35.5878
-5.50007	6.01186 E-4	2.14004 E-2	35.5969
-5.40007	5.99322 E-4	2.13395 E-2	35.6061
-5.30007	5.97467 E-4	2.12789 E-2	35.6152
-5.20007	5.95621 E-4	2.12186 E-2	35.6243
-5.10007	5.93785 E-4	2.11586 E-2	35.6334
-5.00008	5.91958 E-4	2.10989 E-2	35.6425
-4.90008	5.90141 E-4	2.10394 E-2	35.6515
-4.80008	5.88333 E-4	2.09803 E-2	35.6606
-4.70008	5.86534 E-4	2.09214 E-2	35.6696
-4.60008	5.84745 E-4	2.08629 E-2	35.6786
-4.50008	5.82965 E-4	2.08046 E-2	35.6876
-4.40009	5.81193 E-4	2.07466 E-2	35.6966

-4.30009	5.79431 E-4	2.06889 E-2	35.7055
-4.20009	5.77678 E-4	2.06315 E-2	35.7145
-4.10009	5.75933 E-4	2.05743 E-2	35.7234
-4.00009	5.74198 E-4	2.05174 E-2	35.7323
-3.90009	5.72471 E-4	2.04608 E-2	35.7412
-3.80009	5.70753 E-4	2.04045 E-2	35.7501
-3.7001	5.69044 E-4	2.03484 E-2	35.759
-3.6001	5.67343 E-4	2.02926 E-2	35.7678
-3.5001	5.65651 E-4	2.02371 E-2	35.7766
-3.4001	5.63968 E-4	2.01819 E-2	35.7855
-3.3001	5.62293 E-4	2.01269 E-2	35.7943
-3.2001	5.60626 E-4	2.00721 E-2	35.8031
-3.10011	5.58968 E-4	2.00177 E-2	35.8118
-3.00011	5.57318 E-4	1.99635 E-2	35.8206
-2.90011	5.55677 E-4	1.99095 E-2	35.8293
-2.80011	5.54043 E-4	1.98558 E-2	35.8381
-2.70011	5.52418 E-4	1.98024 E-2	35.8468
-2.60011	5.50801 E-4	1.97492 E-2	35.8555
-2.50011	5.49192 E-4	1.96963 E-2	35.8641
-2.40012	5.47591 E-4	1.96436 E-2	35.8728
-2.30012	5.45998 E-4	1.95912 E-2	35.8815
-2.20012	5.44413 E-4	0.019539	35.8901
-2.10012	5.42836 E-4	1.94871 E-2	35.8987
-2.00012	5.41266 E-4	1.94354 E-2	35.9073
-1.90012	5.39705 E-4	0.019384	35.9159
-1.80013	5.38151 E-4	1.93328 E-2	35.9245
-1.70013	5.36605 E-4	1.92818 E-2	35.933
-1.60013	5.35066 E-4	1.92311 E-2	35.9416
-1.50013	5.33535 E-4	1.91806 E-2	35.9501
-1.40013	5.32012 E-4	1.91304 E-2	35.9586
-1.30013	5.30496 E-4	1.90804 E-2	35.9671
-1.20013	5.28988 E-4	1.90306 E-2	35.9756
-1.10014	5.27487 E-4	1.89811 E-2	35.984
-1.00014	5.25993 E-4	1.89318 E-2	35.9925
-0.900139	5.24507 E-4	1.88827 E-2	36.0009
-0.80014	5.23028 E-4	1.88339 E-2	36.0093
-0.700142	5.21557 E-4	1.87853 E-2	36.0177
-0.600143	5.20092 E-4	1.87369 E-2	36.0261
-0.500145	5.18635 E-4	1.86887 E-2	36.0345
-0.400146	5.17184 E-4	1.86408 E-2	36.0429
-0.300148	5.15741 E-4	1.85931 E-2	36.0512
-0.20015	5.14305 E-4	1.85456 E-2	36.0595
-0.100151	5.12876 E-4	1.84983 E-2	36.0679
-1.52588 E-4	5.11454 E-4	1.84513 E-2	36.0761
9.98459 E-2	5.10038 E-4	1.84044 E-2	36.0844
0.199844	5.0863 E-4	1.83578 E-2	36.0927
0.299843	5.07228 E-4	1.83114 E-2	36.101
0.399841	5.05834 E-4	1.82652 E-2	36.1092
0.49984	5.04445 E-4	1.82193 E-2	36.1174
0.599838	5.03064 E-4	1.81735 E-2	36.1256
0.699837	5.01689 E-4	0.018128	36.1338
0.799835	5.00321 E-4	1.80826 E-2	36.142
0.899834	4.9896 E-4	1.80375 E-2	36.1502
0.999832	4.97605 E-4	1.79926 E-2	36.1583
1.09983	4.96256 E-4	1.79478 E-2	36.1664
1.19983	4.94914 E-4	1.79033 E-2	36.1746
1.29983	4.93579 E-4	0.017859	36.1827
1.39983	4.9225 E-4	1.78149 E-2	36.1908
1.49982	4.90927 E-4	0.017771	36.1988
1.59982	4.8961 E-4	1.77273 E-2	36.2069

1.69982	4.883 E-4	1.76838 E-2	36.2149
1.79982	4.86996 E-4	1.76405 E-2	36.223
1.89982	4.85698 E-4	1.75973 E-2	36.231
1.99982	4.84407 E-4	1.75544 E-2	36.239
2.09982	4.83121 E-4	1.75117 E-2	36.247
2.19981	4.81842 E-4	1.74692 E-2	36.255
2.29981	4.80569 E-4	1.74268 E-2	36.2629
2.39981	4.79302 E-4	1.73847 E-2	36.2709
2.49981	4.7804 E-4	1.73427 E-2	36.2788
2.59981	4.76785 E-4	0.017301	36.2867
2.69981	4.75536 E-4	1.72594 E-2	36.2946
2.7998	4.74292 E-4	0.017218	36.3025
2.8998	4.73055 E-4	1.71768 E-2	36.3104
2.9998	4.71823 E-4	1.71358 E-2	36.3182
3.0998	4.70597 E-4	1.70949 E-2	36.3261
3.1998	4.69377 E-4	1.70543 E-2	36.3339
3.2998	4.68163 E-4	1.70138 E-2	36.3417
3.3998	4.66954 E-4	1.69735 E-2	36.3495
3.49979	4.65751 E-4	1.69334 E-2	36.3573
3.59979	4.64553 E-4	1.68935 E-2	36.3651
3.69979	4.63361 E-4	1.68538 E-2	36.3728
3.79979	4.62175 E-4	1.68142 E-2	36.3806
3.89979	4.60994 E-4	1.67748 E-2	36.3883
3.99979	4.59819 E-4	1.67356 E-2	36.396
4.09978	4.58649 E-4	1.66965 E-2	36.4037
4.19978	4.57485 E-4	1.66577 E-2	36.4114
4.29978	4.56326 E-4	0.016619	36.4191
4.39978	4.55172 E-4	1.65804 E-2	36.4267
4.49978	4.54024 E-4	1.65421 E-2	36.4344
4.59978	4.52881 E-4	1.65039 E-2	36.442
4.69978	4.51744 E-4	1.64659 E-2	36.4496
4.79977	4.50611 E-4	0.016428	36.4572
4.89977	4.49484 E-4	1.63904 E-2	36.4648
4.99977	4.48362 E-4	1.63528 E-2	36.4724
5.09977	4.47246 E-4	1.63155 E-2	36.4799
5.19977	4.46134 E-4	1.62783 E-2	36.4875
5.29977	4.45028 E-4	1.62413 E-2	36.495
5.39977	4.43926 E-4	1.62044 E-2	36.5025
5.49976	4.4283 E-4	1.61677 E-2	36.51
5.59976	4.41739 E-4	1.61312 E-2	36.5175
5.69976	4.40652 E-4	1.60948 E-2	36.525
5.79976	4.39571 E-4	1.60586 E-2	36.5324
5.89976	4.38495 E-4	1.60225 E-2	36.5399
5.99976	4.37423 E-4	1.59866 E-2	36.5473
6.09975	4.36357 E-4	1.59509 E-2	36.5547
6.19975	4.35295 E-4	1.59153 E-2	36.5621
6.29975	4.34238 E-4	1.58799 E-2	36.5695
6.39975	4.33186 E-4	1.58446 E-2	36.5769
6.49975	4.32139 E-4	1.58095 E-2	36.5843
6.59975	4.31096 E-4	1.57745 E-2	36.5916
6.69975	4.30059 E-4	1.57397 E-2	36.599
6.79974	4.29026 E-4	0.015705	36.6063
6.89974	4.27997 E-4	1.56705 E-2	36.6136
6.99974	4.26974 E-4	1.56361 E-2	36.6209
7.09974	4.25954 E-4	1.56019 E-2	36.6282
7.19974	4.2494 E-4	1.55679 E-2	36.6354
7.29974	4.2393 E-4	1.55339 E-2	36.6427
7.39973	4.22925 E-4	1.55002 E-2	36.6499
7.49973	4.21924 E-4	1.54665 E-2	36.6572
7.59973	4.20928 E-4	0.015433	36.6644

7.69973	4.19936 E-4	1.53997 E-2	36.6716
7.79973	4.18948 E-4	1.53665 E-2	36.6788
7.89973	4.17965 E-4	1.53334 E-2	36.6859
7.99973	4.16987 E-4	1.53005 E-2	36.6931
8.09972	4.16013 E-4	1.52678 E-2	36.7002
8.19972	4.15043 E-4	1.52351 E-2	36.7074
8.29972	4.14077 E-4	1.52026 E-2	36.7145
8.39972	4.13116 E-4	1.51703 E-2	36.7216
8.49972	4.12159 E-4	1.51381 E-2	36.7287
8.59972	4.11207 E-4	0.015106	36.7358
8.69971	4.10258 E-4	0.015074	36.7428
8.79971	4.09314 E-4	1.50422 E-2	36.7499
8.89971	4.08374 E-4	1.50106 E-2	36.7569
8.99971	4.07438 E-4	0.014979	36.7639
9.09971	4.06507 E-4	1.49476 E-2	36.7709
9.19971	4.05579 E-4	1.49164 E-2	36.7779
9.29971	4.04656 E-4	1.48852 E-2	36.7849
9.3997	4.03737 E-4	1.48542 E-2	36.7919
9.4997	4.02821 E-4	1.48234 E-2	36.7989
9.5997	4.0191 E-4	1.47926 E-2	36.8058
9.6997	4.01003 E-4	0.014762	36.8127
9.7997	4.001 E-4	1.47315 E-2	36.8196
9.8997	3.99201 E-4	1.47012 E-2	36.8266
9.99969	3.98305 E-4	0.014671	36.8335
10.0997	3.97414 E-4	1.46409 E-2	36.8403
10.1997	3.96527 E-4	1.46109 E-2	36.8472
10.2997	3.95643 E-4	1.45811 E-2	36.8541
10.3997	3.94764 E-4	1.45513 E-2	36.8609
10.4997	3.93888 E-4	1.45217 E-2	36.8677
10.5997	3.93016 E-4	1.44923 E-2	36.8745
10.6997	3.92148 E-4	1.44629 E-2	36.8813
10.7997	3.91283 E-4	1.44337 E-2	36.8881
10.8997	3.90423 E-4	1.44046 E-2	36.8949
10.9997	3.89566 E-4	1.43756 E-2	36.9017
11.0997	3.88713 E-4	1.43468 E-2	36.9084
11.1997	3.87864 E-4	0.014318	36.9151
11.2997	3.87018 E-4	1.42894 E-2	36.9219
11.3997	3.86176 E-4	1.42609 E-2	36.9286
11.4997	3.85338 E-4	1.42325 E-2	36.9353
11.5997	3.84503 E-4	1.42043 E-2	36.942
11.6997	3.83672 E-4	1.41761 E-2	36.9486
11.7997	3.82844 E-4	1.41481 E-2	36.9553
11.8997	3.82021 E-4	1.41202 E-2	36.9619
11.9997	3.812 E-4	1.40924 E-2	36.9686
12.0997	3.80383 E-4	1.40647 E-2	36.9752
12.1997	3.7957 E-4	1.40372 E-2	36.9818
12.2997	3.7876 E-4	1.40097 E-2	36.9884
12.3997	3.77954 E-4	1.39824 E-2	36.995
12.4997	3.77151 E-4	1.39552 E-2	37.0015
12.5997	3.76352 E-4	1.39281 E-2	37.0081
12.6997	3.75556 E-4	1.39011 E-2	37.0146
12.7997	3.74764 E-4	1.38742 E-2	37.0212
12.8997	3.73974 E-4	1.38474 E-2	37.0277
12.9996	3.73189 E-4	1.38207 E-2	37.0342
13.0996	3.72406 E-4	1.37942 E-2	37.0407
13.1996	3.71627 E-4	1.37677 E-2	37.0472
13.2996	3.70852 E-4	1.37414 E-2	37.0536
13.3996	3.70079 E-4	1.37152 E-2	37.0601
13.4996	3.6931 E-4	1.36891 E-2	37.0665
13.5996	3.68545 E-4	0.013663	37.073

13.6996	3.67782 E-4	1.36371 E-2	37.0794
13.7996	3.67023 E-4	1.36113 E-2	37.0858
13.8996	3.66267 E-4	1.35856 E-2	37.0922
13.9996	3.65514 E-4	0.01356	37.0985
14.0996	3.64764 E-4	1.35345 E-2	37.1049
14.1996	3.64018 E-4	1.35092 E-2	37.1113
14.2996	3.63274 E-4	1.34839 E-2	37.1176
14.3996	3.62534 E-4	1.34587 E-2	37.1239
14.4996	3.61797 E-4	1.34336 E-2	37.1303
14.5996	3.61063 E-4	1.34087 E-2	37.1366
14.6996	3.60333 E-4	1.33838 E-2	37.1429
14.7996	3.59605 E-4	0.013359	37.1491
14.8996	3.5888 E-4	1.33343 E-2	37.1554
14.9996	3.58159 E-4	1.33098 E-2	37.1617
15.0996	3.5744 E-4	1.32853 E-2	37.1679
15.1996	3.56725 E-4	1.32609 E-2	37.1741
15.2996	3.56012 E-4	1.32367 E-2	37.1804
15.3996	3.55303 E-4	1.32125 E-2	37.1866
15.4996	3.54596 E-4	1.31884 E-2	37.1928
15.5996	3.53892 E-4	1.31644 E-2	37.1989
15.6996	3.53192 E-4	1.31405 E-2	37.2051
15.7996	3.52494 E-4	1.31168 E-2	37.2113
15.8996	3.51799 E-4	1.30931 E-2	37.2174
15.9996	3.51108 E-4	1.30695 E-2	37.2236
16.0996	3.50419 E-4	0.013046	37.2297
16.1996	3.49732 E-4	1.30226 E-2	37.2358
16.2996	3.49049 E-4	1.29993 E-2	37.2419
16.3996	3.48369 E-4	0.012976	37.248
16.4996	3.47691 E-4	1.29529 E-2	37.2541
16.5996	3.47017 E-4	1.29299 E-2	37.2601
16.6996	3.46345 E-4	1.29069 E-2	37.2662
16.7996	3.45675 E-4	1.28841 E-2	37.2722
16.8996	3.45009 E-4	1.28613 E-2	37.2782
16.9996	3.44345 E-4	1.28387 E-2	37.2842
17.0996	3.43685 E-4	1.28161 E-2	37.2902
17.1996	3.43026 E-4	1.27936 E-2	37.2962
17.2996	3.42371 E-4	1.27712 E-2	37.3022
17.3996	3.41718 E-4	1.27489 E-2	37.3082
17.4996	3.41068 E-4	1.27267 E-2	37.3141
17.5996	3.40421 E-4	1.27045 E-2	37.3201
17.6996	3.39777 E-4	1.26825 E-2	37.326
17.7996	3.39135 E-4	1.26605 E-2	37.3319
17.8996	3.38495 E-4	1.26387 E-2	37.3378
17.9996	3.37859 E-4	1.26169 E-2	37.3437
18.0996	3.37224 E-4	1.25952 E-2	37.3496
18.1996	3.36593 E-4	1.25736 E-2	37.3555
18.2996	3.35964 E-4	1.25521 E-2	37.3613
18.3996	3.35338 E-4	1.25306 E-2	37.3672
18.4996	3.34714 E-4	1.25093 E-2	37.373
18.5996	3.34093 E-4	0.012488	37.3788
18.6996	3.33474 E-4	1.24668 E-2	37.3847
18.7996	3.32858 E-4	1.24457 E-2	37.3904
18.8996	3.32245 E-4	1.24247 E-2	37.3962
18.9996	3.31634 E-4	1.24038 E-2	37.402
19.0996	3.31025 E-4	1.23829 E-2	37.4078
19.1996	3.30419 E-4	1.23621 E-2	37.4135
19.2996	3.29815 E-4	1.23415 E-2	37.4193
19.3996	3.29214 E-4	1.23208 E-2	37.425
19.4995	3.28615 E-4	1.23003 E-2	37.4307
19.5995	3.28019 E-4	1.22799 E-2	37.4364

19.6995	3.27425 E-4	1.22595 E-2	37.4421
19.7995	3.26834 E-4	1.22392 E-2	37.4478
19.8995	3.26245 E-4	0.012219	37.4535
19.9995	3.25658 E-4	1.21989 E-2	37.4592
20.0995	3.25074 E-4	1.21788 E-2	37.4648
20.1995	3.24492 E-4	1.21589 E-2	37.4704
20.2995	3.23913 E-4	0.012139	37.4761
20.3995	3.23335 E-4	1.21192 E-2	37.4817
20.4995	3.2276 E-4	1.20994 E-2	37.4873
20.5995	3.22188 E-4	1.20798 E-2	37.4929
20.6995	3.21618 E-4	1.20602 E-2	37.4985
20.7995	3.2105 E-4	1.20407 E-2	37.504
20.8995	3.20484 E-4	1.20212 E-2	37.5096
20.9995	3.19921 E-4	1.20019 E-2	37.5151
21.0995	3.1936 E-4	1.19826 E-2	37.5207
21.1995	3.18801 E-4	1.19634 E-2	37.5262
21.2995	3.18244 E-4	1.19443 E-2	37.5317
21.3995	3.1769 E-4	1.19252 E-2	37.5372
21.4995	3.17138 E-4	1.19062 E-2	37.5427
21.5995	3.16588 E-4	1.18873 E-2	37.5482
21.6995	3.1604 E-4	1.18685 E-2	37.5537
21.7995	3.15495 E-4	1.18497 E-2	37.5591
21.8995	3.14951 E-4	0.011831	37.5646
21.9995	3.1441 E-4	1.18124 E-2	37.57
22.0995	3.13871 E-4	1.17938 E-2	37.5754
22.1995	3.13334 E-4	1.17754 E-2	37.5809
22.2995	3.128 E-4	0.011757	37.5862
22.3995	3.12267 E-4	1.17386 E-2	37.5916
22.4995	3.11737 E-4	1.17204 E-2	37.597
22.5995	3.11208 E-4	1.17022 E-2	37.6024
22.6995	3.10682 E-4	1.16841 E-2	37.6077
22.7995	3.10158 E-4	0.011666	37.6131
22.8995	3.09636 E-4	0.011648	37.6184
22.9995	3.09116 E-4	1.16301 E-2	37.6238
23.0995	3.08598 E-4	1.16123 E-2	37.6291
23.1995	3.08082 E-4	1.15945 E-2	37.6344
23.2995	3.07569 E-4	1.15768 E-2	37.6397
23.3995	3.07057 E-4	1.15591 E-2	37.6449
23.4995	3.06547 E-4	1.15416 E-2	37.6502
23.5995	3.06039 E-4	1.15241 E-2	37.6555
23.6995	3.05534 E-4	1.15066 E-2	37.6607
23.7995	3.0503 E-4	1.14892 E-2	37.666
23.8995	3.04528 E-4	1.14719 E-2	37.6712
23.9995	3.04029 E-4	1.14547 E-2	37.6764
24.0995	3.03531 E-4	1.14375 E-2	37.6816
24.1995	3.03035 E-4	1.14204 E-2	37.6868
24.2995	3.02541 E-4	1.14034 E-2	37.692
24.3995	3.02049 E-4	1.13864 E-2	37.6972
24.4995	3.01559 E-4	1.13695 E-2	37.7023
24.5995	3.01071 E-4	1.13526 E-2	37.7075
24.6995	3.00585 E-4	1.13359 E-2	37.7126
24.7995	3.00101 E-4	1.13191 E-2	37.7177
24.8995	2.99619 E-4	1.13025 E-2	37.7228
24.9995	2.99138 E-4	1.12859 E-2	37.7279
25.0995	2.9866 E-4	1.12693 E-2	37.733
25.1995	2.98183 E-4	1.12529 E-2	37.7381
25.2995	2.97709 E-4	1.12365 E-2	37.7432
25.3995	2.97236 E-4	1.12201 E-2	37.7483
25.4995	2.96765 E-4	1.12039 E-2	37.7533
[illegible]	2.96295 E-4	1.11876 E-2	37.7584

25.6995	2.95828 E-4	1.11715 E-2	37.7634
25.7995	2.95363 E-4	1.11554 E-2	37.7684
25.8995	2.94899 E-4	1.11393 E-2	37.7734
25.9995	2.94437 E-4	1.11234 E-2	37.7784
26.0994	2.93977 E-4	1.11074 E-2	37.7834
26.1994	2.93518 E-4	1.10916 E-2	37.7884
26.2994	2.93062 E-4	1.10758 E-2	37.7934
26.3994	2.92607 E-4	1.10601 E-2	37.7983
26.4994	2.92154 E-4	1.10444 E-2	37.8033
26.5994	2.91703 E-4	1.10288 E-2	37.8082
26.6994	2.91254 E-4	1.10132 E-2	37.8131
26.7994	2.90806 E-4	1.09977 E-2	37.8181
26.8994	2.9036 E-4	1.09823 E-2	37.823
26.9994	2.89916 E-4	1.09669 E-2	37.8279
27.0994	2.89473 E-4	1.09516 E-2	37.8328
27.1994	2.89032 E-4	1.09363 E-2	37.8376
27.2994	2.88593 E-4	1.09211 E-2	37.8425
27.3994	2.88156 E-4	1.09059 E-2	37.8473
27.4994	2.8772 E-4	1.08908 E-2	37.8522
27.5994	2.87286 E-4	1.08758 E-2	37.857
27.6994	2.86854 E-4	1.08608 E-2	37.8618
27.7994	2.86423 E-4	1.08459 E-2	37.8667
27.8994	2.85994 E-4	0.010831	37.8715
27.9994	2.85567 E-4	1.08162 E-2	37.8763
28.0994	2.85141 E-4	1.08014 E-2	37.881
28.1994	2.84717 E-4	1.07867 E-2	37.8858
28.2994	2.84295 E-4	1.07721 E-2	37.8906
28.3994	2.83874 E-4	1.07575 E-2	37.8953
28.4994	2.83455 E-4	0.010743	37.9001
28.5994	2.83037 E-4	1.07285 E-2	37.9048
28.6994	2.82621 E-4	0.010714	37.9095
28.7994	2.82207 E-4	1.06997 E-2	37.9142
28.8994	2.81794 E-4	1.06853 E-2	37.9189
28.9994	2.81383 E-4	1.06711 E-2	37.9236
29.0994	2.80973 E-4	1.06568 E-2	37.9283
29.1994	2.80565 E-4	1.06427 E-2	37.933
29.2994	2.80159 E-4	1.06286 E-2	37.9376
29.3994	2.79754 E-4	1.06145 E-2	37.9423
29.4994	2.79351 E-4	1.06005 E-2	37.9469
29.5994	2.78949 E-4	1.05865 E-2	37.9515
29.6994	2.78549 E-4	1.05726 E-2	37.9562
29.7994	2.7815 E-4	1.05588 E-2	37.9608
29.8994	2.77753 E-4	0.010545	37.9654
29.9994	2.77357 E-4	1.05312 E-2	37.97
30.0994	2.76963 E-4	1.05175 E-2	37.9746
30.1994	2.7657 E-4	1.05039 E-2	37.9791
30.2994	2.76179 E-4	1.04903 E-2	37.9837
30.3994	2.75789 E-4	1.04768 E-2	37.9882
30.4994	2.75401 E-4	1.04633 E-2	37.9928
30.5994	2.75015 E-4	1.04498 E-2	37.9973
30.6994	2.74629 E-4	1.04364 E-2	38.0018
30.7994	2.74246 E-4	1.04231 E-2	38.0063
30.8994	2.73863 E-4	1.04098 E-2	38.0108
30.9994	2.73482 E-4	1.03965 E-2	38.0153
31.0994	2.73103 E-4	1.03833 E-2	38.0198
31.1994	2.72725 E-4	1.03702 E-2	38.0243
31.2994	2.72349 E-4	1.03571 E-2	38.0287
31.3994	2.71974 E-4	0.010344	38.0332
31.4994	2.716 E-4	0.010331	38.0376
31.5994	2.71228 E-4	1.03181 E-2	38.0421

31.6994	2.70857 E-4	1.03052 E-2	38.0465
31.7994	2.70488 E-4	1.02923 E-2	38.0509
31.8994	2.7012 E-4	1.02795 E-2	38.0553
31.9994	2.69753 E-4	1.02667 E-2	38.0597
32.0994	2.69388 E-4	0.010254	38.0641
32.1994	2.69024 E-4	1.02413 E-2	38.0685
32.2994	2.68661 E-4	1.02287 E-2	38.0728
32.3994	2.683 E-4	1.02161 E-2	38.0772
32.4994	2.67941 E-4	1.02036 E-2	38.0815
32.5993	2.67582 E-4	1.01911 E-2	38.0858
32.6993	2.67225 E-4	1.01787 E-2	38.0902
32.7993	2.6687 E-4	1.01663 E-2	38.0945
32.8993	2.66515 E-4	1.01539 E-2	38.0988
32.9993	2.66162 E-4	1.01416 E-2	38.1031
33.0993	2.65811 E-4	1.01294 E-2	38.1074
33.1993	2.6546 E-4	1.01171 E-2	38.1117
33.2993	2.65111 E-4	0.010105	38.1159
33.3993	2.64764 E-4	1.00928 E-2	38.1202
33.4993	2.64417 E-4	1.00808 E-2	38.1244
33.5993	2.64072 E-4	1.00687 E-2	38.1287
33.6993	2.63729 E-4	1.00567 E-2	38.1329
33.7993	2.63386 E-4	1.00448 E-2	38.1371
33.8993	2.63045 E-4	1.00329 E-2	38.1413
33.9993	2.62705 E-4	0.010021	38.1455
34.0993	2.62367 E-4	1.00092 E-2	38.1497
34.1993	2.62029 E-4	9.99744 E-3	38.1539
34.2993	2.61693 E-4	9.98571 E-3	38.1581
34.3993	2.61358 E-4	9.97402 E-3	38.1622
34.4993	2.61025 E-4	9.96238 E-3	38.1664
34.5993	2.60693 E-4	9.95078 E-3	38.1705
34.6993	2.60362 E-4	9.93922 E-3	38.1747
34.7993	2.60032 E-4	9.9277 E-3	38.1788
34.8993	2.59703 E-4	9.91623 E-3	38.1829
34.9993	2.59376 E-4	9.9048 E-3	38.187
35.0993	2.5905 E-4	9.8934 E-3	38.1911
35.1993	2.58725 E-4	9.88206 E-3	38.1952
35.2993	2.58401 E-4	9.87075 E-3	38.1993
35.3993	2.58079 E-4	9.85948 E-3	38.2034
35.4993	2.57758 E-4	9.84826 E-3	38.2074
35.5993	2.57438 E-4	9.83707 E-3	38.2115
35.6993	2.57119 E-4	9.82593 E-3	38.2155
35.7993	2.56801 E-4	9.81483 E-3	38.2196
35.8993	2.56485 E-4	9.80377 E-3	38.2236
35.9993	2.56169 E-4	9.79274 E-3	38.2276
36.0993	2.55855 E-4	9.78176 E-3	38.2316
36.1993	2.55542 E-4	9.77082 E-3	38.2356
36.2993	2.55231 E-4	9.75992 E-3	38.2396
36.3993	2.5492 E-4	9.74906 E-3	38.2436
36.4993	2.54611 E-4	9.73823 E-3	38.2475
36.5993	2.54302 E-4	9.72745 E-3	38.2515
36.6993	2.53995 E-4	9.71671 E-3	38.2555
36.7993	2.53689 E-4	0.009706	38.2594
36.8993	2.53385 E-4	9.69534 E-3	38.2633
36.9993	2.53081 E-4	9.68471 E-3	38.2673
37.0993	2.52778 E-4	9.67412 E-3	38.2712
37.1993	2.52477 E-4	9.66357 E-3	38.2751
37.2993	2.52177 E-4	9.65306 E-3	38.279
37.3993	2.51877 E-4	9.64259 E-3	38.2829
37.4993	2.51579 E-4	9.63216 E-3	38.2868
37.5993	2.51282 E-4	9.62176 E-3	38.2906

37.6993	2.50987 E-4	9.6114 E-3	38.2945
37.7993	2.50692 E-4	9.60108 E-3	38.2983
37.8993	2.50398 E-4	9.5908 E-3	38.3022
37.9993	2.50106 E-4	9.58055 E-3	38.306
38.0993	2.49814 E-4	9.57034 E-3	38.3098
38.1993	2.49524 E-4	9.56017 E-3	38.3137
38.2993	2.49235 E-4	9.55004 E-3	38.3175
38.3993	2.48946 E-4	9.53994 E-3	38.3213
38.4993	2.48659 E-4	9.52988 E-3	38.3251
38.5993	2.48373 E-4	9.51985 E-3	38.3288
38.6993	2.48088 E-4	9.50987 E-3	38.3326
38.7993	2.47804 E-4	9.49991 E-3	38.3364
38.8993	2.47521 E-4	0.00949	38.3401
38.9993	2.47239 E-4	9.48012 E-3	38.3439
39.0993	2.46959 E-4	9.47027 E-3	38.3476
39.1992	2.46679 E-4	9.46047 E-3	38.3513
39.2992	2.464 E-4	9.45069 E-3	38.3551
39.3992	2.46123 E-4	9.44096 E-3	38.3588
39.4992	2.45846 E-4	9.43125 E-3	38.3625
39.5992	2.4557 E-4	9.42159 E-3	38.3662
39.6992	2.45296 E-4	9.41196 E-3	38.3699
39.7992	2.45022 E-4	9.40236 E-3	38.3735
39.8992	2.4475 E-4	9.3928 E-3	38.3772
39.9992	2.44478 E-4	9.38327 E-3	38.3808
40.0992	2.44207 E-4	9.37378 E-3	38.3845
40.1992	2.43938 E-4	9.36432 E-3	38.3881
40.2992	2.43669 E-4	9.3549 E-3	38.3918
40.3992	2.43402 E-4	9.34551 E-3	38.3954
40.4992	2.43135 E-4	9.33616 E-3	38.399
40.5992	2.4287 E-4	9.32684 E-3	38.4026
40.6992	2.42605 E-4	9.31755 E-3	38.4062
40.7992	2.42342 E-4	9.30829 E-3	38.4098
40.8992	2.42079 E-4	9.29907 E-3	38.4134
40.9992	2.41817 E-4	9.28989 E-3	38.417
41.0992	2.41557 E-4	9.28073 E-3	38.4205
41.1992	2.41297 E-4	9.27161 E-3	38.4241
41.2992	2.41038 E-4	9.26253 E-3	38.4276
41.3992	2.4078 E-4	9.25347 E-3	38.4312
41.4992	2.40524 E-4	9.24445 E-3	38.4347
41.5992	2.40268 E-4	9.23546 E-3	38.4382
41.6992	2.40013 E-4	9.22651 E-3	38.4417
41.7992	2.39759 E-4	9.21759 E-3	38.4453
41.8992	2.39506 E-4	9.20869 E-3	38.4487
41.9992	2.39254 E-4	9.19984 E-3	38.4522
42.0992	2.39002 E-4	9.19101 E-3	38.4557
42.1992	2.38752 E-4	9.18221 E-3	38.4592
42.2992	2.38503 E-4	9.17345 E-3	38.4627
42.3992	2.38254 E-4	9.16472 E-3	38.4661
42.4992	2.38007 E-4	9.15602 E-3	38.4695
42.5992	2.3776 E-4	9.14736 E-3	38.473
42.6992	2.37515 E-4	9.13872 E-3	38.4764
42.7992	2.3727 E-4	9.13011 E-3	38.4798
42.8992	2.37026 E-4	9.12154 E-3	38.4833
42.9992	2.36783 E-4	0.009113	38.4867
43.0992	2.36541 E-4	9.10449 E-3	38.4901
43.1992	2.363 E-4	9.09601 E-3	38.4934
43.2992	2.36060 E-4	9.08756 E-3	38.4968
43.3992	2.35821 E-4	9.07914 E-3	38.5002
43.4992	2.35582 E-4	9.07075 E-3	38.5036
43.5992	2.35345 E-4	9.06239 E-3	38.5069

43.6992	2.35108 E-4	9.05407 E-3	38.5103
43.7992	2.34872 E-4	9.04577 E-3	38.5136
43.8992	2.34637 E-4	9.0375 E-3	38.5169
43.9992	2.34403 E-4	9.02927 E-3	38.5203
44.0992	2.3417 E-4	9.02106 E-3	38.5236
44.1992	2.33938 E-4	9.01288 E-3	38.5269
44.2992	2.33706 E-4	9.00473 E-3	38.5302
44.3992	2.33475 E-4	8.99662 E-3	38.5335
44.4992	2.33246 E-4	8.98853 E-3	38.5368
44.5992	2.33017 E-4	8.98047 E-3	38.54
44.6992	2.32789 E-4	8.97244 E-3	38.5433
44.7992	2.32561 E-4	8.96444 E-3	38.5465
44.8992	2.32335 E-4	8.95647 E-3	38.5498
44.9992	2.32109 E-4	8.94853 E-3	38.553
45.0992	2.31885 E-4	8.94061 E-3	38.5563
45.1992	2.31661 E-4	8.93273 E-3	38.5595
45.2992	2.31438 E-4	8.92487 E-3	38.5627
45.3992	2.31216 E-4	8.91704 E-3	38.5659
45.4992	2.30994 E-4	8.90924 E-3	38.5691
45.5992	2.30774 E-4	8.90147 E-3	38.5723
45.6992	2.30554 E-4	8.89373 E-3	38.5755
45.7991	2.30335 E-4	8.88602 E-3	38.5787
45.8991	2.30117 E-4	8.87833 E-3	38.5818
45.9991	2.299 E-4	8.87067 E-3	38.585
46.0991	2.29683 E-4	8.86304 E-3	38.5882
46.1991	2.29467 E-4	8.85544 E-3	38.5913
46.2991	2.29252 E-4	8.84787 E-3	38.5944
46.3991	2.29038 E-4	8.84032 E-3	38.5976
46.4991	2.28825 E-4	8.8328 E-3	38.6007
46.5991	2.28612 E-4	8.82531 E-3	38.6038
46.6991	2.28401 E-4	8.81785 E-3	38.6069
46.7991	2.2819 E-4	8.81041 E-3	38.61
46.8991	2.2798 E-4	0.008803	38.6131
46.9991	2.2777 E-4	8.79562 E-3	38.6162
47.0991	2.27562 E-4	8.78826 E-3	38.6193
47.1991	2.27354 E-4	8.78093 E-3	38.6223
47.2991	2.27147 E-4	8.77363 E-3	38.6254
47.3991	2.2694 E-4	8.76635 E-3	38.6284
47.4991	2.26735 E-4	8.7591 E-3	38.6315
47.5991	2.2653 E-4	8.75188 E-3	38.6345
47.6991	2.26326 E-4	8.74468 E-3	38.6375
47.7991	2.26123 E-4	8.73752 E-3	38.6406
47.8991	2.2592 E-4	8.73037 E-3	38.6436
47.9991	2.25719 E-4	8.72326 E-3	38.6466
48.0991	2.25518 E-4	8.71616 E-3	38.6496
48.1991	2.25317 E-4	8.7091 E-3	38.6526
48.2991	2.25118 E-4	8.70206 E-3	38.6556
48.3991	2.24919 E-4	8.69505 E-3	38.6585
48.4991	2.24721 E-4	8.68806 E-3	38.6615
48.5991	2.24524 E-4	8.6811 E-3	38.6645
48.6991	2.24327 E-4	8.67416 E-3	38.6674
48.7991	2.24132 E-4	8.66725 E-3	38.6704
48.8991	2.23937 E-4	8.66036 E-3	38.6733
48.9991	2.23742 E-4	8.6535 E-3	38.6762
49.0991	2.23549 E-4	8.64667 E-3	38.6791
49.1991	2.23356 E-4	8.63986 E-3	38.682
49.2991	2.23163 E-4	8.63307 E-3	38.685
49.3991	2.22972 E-4	8.62631 E-3	38.6879
49.4991	2.22781 E-4	8.61958 E-3	38.6908
49.5991	2.22591 E-4	8.61287 E-3	38.6936

49.6991	2.22402 E-4	8.60618 E-3	38.6965
49.7991	2.22213 E-4	8.59952 E-3	38.6994
49.8991	2.22025 E-4	8.59288 E-3	38.7022
49.9991	2.21838 E-4	8.58627 E-3	38.7051
50.0991	2.21652 E-4	8.57968 E-3	38.7079
50.1991	2.21466 E-4	8.57312 E-3	38.7108
50.2991	2.21281 E-4	8.56658 E-3	38.7136
50.3991	2.21096 E-4	8.56006 E-3	38.7164
50.4991	2.20913 E-4	8.55357 E-3	38.7192
50.5991	2.2073 E-4	8.54711 E-3	38.722
50.6991	2.20547 E-4	8.54066 E-3	38.7249
50.7991	2.20366 E-4	8.53424 E-3	38.7276
50.8991	2.20185 E-4	8.52785 E-3	38.7304
50.9991	2.20004 E-4	8.52148 E-3	38.7332
51.0991	2.19825 E-4	8.51513 E-3	38.736
51.1991	2.19646 E-4	8.5088 E-3	38.7387
51.2991	2.19468 E-4	8.5025 E-3	38.7415
51.3991	2.1929 E-4	8.49622 E-3	38.7442
51.4991	2.19113 E-4	8.48997 E-3	38.747
51.5991	2.18937 E-4	8.48374 E-3	38.7497
51.6991	2.18761 E-4	8.47753 E-3	38.7525
51.7991	2.18586 E-4	8.47134 E-3	38.7552
51.8991	2.18412 E-4	8.46518 E-3	38.7579
51.9991	2.18238 E-4	8.45904 E-3	38.7606
52.0991	2.18065 E-4	8.45293 E-3	38.7633
52.1991	2.17893 E-4	8.44683 E-3	38.766
52.299	2.17721 E-4	8.44076 E-3	38.7687
52.399	2.1755 E-4	8.43471 E-3	38.7713
52.499	2.1738 E-4	8.42869 E-3	38.774
52.599	2.1721 E-4	8.42268 E-3	38.7767
52.699	2.17041 E-4	8.4167 E-3	38.7793
52.799	2.16873 E-4	8.41075 E-3	38.782
52.899	2.16705 E-4	8.40481 E-3	38.7846
52.999	2.16537 E-4	8.3989 E-3	38.7873
53.099	2.16371 E-4	0.008393	38.7899
53.199	2.16205 E-4	8.38713 E-3	38.7925
53.299	2.1604 E-4	8.38129 E-3	38.7951
53.399	2.15875 E-4	8.37546 E-3	38.7977
53.499	2.15711 E-4	8.36966 E-3	38.8003
53.599	2.15548 E-4	8.36387 E-3	38.8029
53.699	2.15385 E-4	8.35811 E-3	38.8055
53.799	2.15223 E-4	8.35237 E-3	38.8081
53.899	2.15061 E-4	8.34666 E-3	38.8106
53.999	2.149 E-4	8.34096 E-3	38.8132
54.099	2.1474 E-4	8.33528 E-3	38.8157
54.199	2.1458 E-4	8.32963 E-3	38.8183
54.299	2.14421 E-4	0.008324	38.8208
54.399	2.14262 E-4	8.31839 E-3	38.8234
54.499	2.14104 E-4	8.3128 E-3	38.8259
54.599	2.13947 E-4	8.30723 E-3	38.8284
54.699	2.1379 E-4	8.30168 E-3	38.8309
54.799	2.13634 E-4	8.29616 E-3	38.8334
54.899	2.13479 E-4	8.29065 E-3	38.8359
54.999	2.13324 E-4	8.28517 E-3	38.8384
55.099	2.1317 E-4	8.2797 E-3	38.8409
55.199	2.13016 E-4	8.27426 E-3	38.8434
55.299	2.12863 E-4	8.26884 E-3	38.8459
55.399	2.1271 E-4	8.26344 E-3	38.8483
55.499	2.12558 E-4	8.25805 E-3	38.8508
55.599	2.12407 E-4	8.25269 E-3	38.8532

55.699	2.12256 E-4	8.24735 E-3	38.8557
55.799	2.12106 E-4	8.24203 E-3	38.8581
55.899	2.11956 E-4	8.23673 E-3	38.8606
55.999	2.11807 E-4	8.23145 E-3	38.863
56.099	2.11659 E-4	8.22619 E-3	38.8654
56.199	2.11511 E-4	8.22096 E-3	38.8678
56.299	2.11363 E-4	8.21573 E-3	38.8702
56.399	2.11217 E-4	8.21054 E-3	38.8726
56.499	2.1107 E-4	8.20536 E-3	38.875
56.599	2.10925 E-4	8.2002 E-3	38.8774
56.699	2.1078 E-4	8.19506 E-3	38.8797
56.799	2.10635 E-4	8.18994 E-3	38.8821
56.899	2.10491 E-4	8.18484 E-3	38.8845
56.999	2.10348 E-4	8.17975 E-3	38.8868
57.099	2.10205 E-4	8.17469 E-3	38.8892
57.199	2.10063 E-4	8.16965 E-3	38.8915
57.299	2.09921 E-4	8.16463 E-3	38.8939
57.399	2.0978 E-4	8.15962 E-3	38.8962
57.499	2.09639 E-4	8.15464 E-3	38.8985
57.599	2.09499 E-4	8.14968 E-3	38.9008
57.699	2.09359 E-4	8.14473 E-3	38.9031
57.799	2.0922 E-4	8.1398 E-3	38.9054
57.899	2.09082 E-4	8.1349 E-3	38.9077
57.999	2.08944 E-4	8.13001 E-3	38.91
58.099	2.08806 E-4	8.12514 E-3	38.9123
58.199	2.0867 E-4	8.12029 E-3	38.9146
58.299	2.08533 E-4	8.11546 E-3	38.9168
58.399	2.08397 E-4	8.11064 E-3	38.9191
58.499	2.08262 E-4	8.10585 E-3	38.9214
58.599	2.08128 E-4	8.10107 E-3	38.9236
58.699	2.07993 E-4	8.09632 E-3	38.9259
58.799	2.0786 E-4	8.09158 E-3	38.9281
58.8989	2.07727 E-4	8.08686 E-3	38.9303
58.9989	2.07594 E-4	8.08216 E-3	38.9325
59.0989	2.07462 E-4	8.07747 E-3	38.9347
59.1989	2.0733 E-4	8.07281 E-3	38.937
59.2989	2.07199 E-4	8.06816 E-3	38.9392
59.3989	2.07069 E-4	8.06353 E-3	38.9413
59.4989	2.06939 E-4	8.05892 E-3	38.9435
59.5989	2.06809 E-4	8.05433 E-3	38.9457
59.6989	2.0668 E-4	8.04976 E-3	38.9479
59.7989	2.06552 E-4	8.0452 E-3	38.9501
59.8989	2.06424 E-4	8.04066 E-3	38.9522
59.9989	2.06296 E-4	8.03614 E-3	38.9544
60.0989	2.06169 E-4	8.03164 E-3	38.9565
60.1989	2.06043 E-4	8.02716 E-3	38.9587
60.2989	2.05917 E-4	8.02269 E-3	38.9608
60.3989	2.05791 E-4	8.01824 E-3	38.963
60.4989	2.05666 E-4	8.01381 E-3	38.9651
60.5989	2.05542 E-4	8.0094 E-3	38.9672
60.6989	2.05418 E-4	0.008005	38.9693
60.7989	2.05295 E-4	8.00062 E-3	38.9714
60.8989	2.05172 E-4	7.99626 E-3	38.9735
60.9989	2.05049 E-4	7.99192 E-3	38.9756
61.0989	2.04927 E-4	7.98759 E-3	38.9777
61.1989	2.04806 E-4	7.98328 E-3	38.9798
61.2989	2.04685 E-4	7.97899 E-3	38.9818
61.3989	2.04564 E-4	7.97472 E-3	38.9839
61.4989	2.04444 E-4	7.97046 E-3	38.986
61.5989	2.04325 E-4	7.96622 E-3	38.988

61.6989	2.04206 E-4	7.96199 E-3	38.9901
61.7989	2.04087 E-4	7.95779 E-3	38.9921
61.8989	2.03969 E-4	7.9536 E-3	38.9942
61.9989	2.03851 E-4	7.94943 E-3	38.9962
62.0989	2.03734 E-4	7.94527 E-3	38.9982
62.1989	2.03618 E-4	7.94113 E-3	39.0002
62.2989	2.03501 E-4	7.93701 E-3	39.0022
62.3989	2.03386 E-4	7.93291 E-3	39.0043
62.4989	2.0327 E-4	7.92882 E-3	39.0062
62.5989	2.03156 E-4	7.92474 E-3	39.0082
62.6989	2.03041 E-4	7.92069 E-3	39.0102
62.7989	2.02928 E-4	7.91665 E-3	39.0122
62.8989	2.02814 E-4	7.91263 E-3	39.0142
62.9989	2.02701 E-4	7.90862 E-3	39.0161
63.0989	2.02589 E-4	7.90463 E-3	39.0181
63.1989	2.02477 E-4	7.90066 E-3	39.0201
63.2989	2.02365 E-4	7.8967 E-3	39.022
63.3989	2.02254 E-4	7.89276 E-3	39.024
63.4989	2.02144 E-4	7.88884 E-3	39.0259
63.5989	2.02033 E-4	7.88493 E-3	39.0278
63.6989	2.01924 E-4	7.88103 E-3	39.0297
63.7989	2.01815 E-4	7.87716 E-3	39.0317
63.8989	2.01706 E-4	7.8733 E-3	39.0336
63.9989	2.01597 E-4	7.86945 E-3	39.0355
64.0989	2.0149 E-4	7.86563 E-3	39.0374
64.1989	2.01382 E-4	7.86181 E-3	39.0393
64.2989	2.01275 E-4	7.85802 E-3	39.0412
64.3989	2.01169 E-4	7.85423 E-3	39.043
64.4989	2.01062 E-4	7.85047 E-3	39.0449
64.5989	2.00957 E-4	7.84672 E-3	39.0468
64.6989	2.00852 E-4	7.84299 E-3	39.0487
64.7989	2.00747 E-4	7.83927 E-3	39.0505
64.8989	2.00643 E-4	7.83557 E-3	39.0524
64.9989	2.00539 E-4	7.83188 E-3	39.0542
65.0989	2.00435 E-4	7.82821 E-3	39.0561
65.1989	2.00332 E-4	7.82455 E-3	39.0579
65.2989	2.0023 E-4	7.82091 E-3	39.0597
65.3988	2.00127 E-4	7.81729 E-3	39.0615
65.4988	2.00026 E-4	7.81367 E-3	39.0633
65.5988	1.99924 E-4	7.81008 E-3	39.0652
65.6988	1.99824 E-4	7.8065 E-3	39.067
65.7988	1.99723 E-4	7.80294 E-3	39.0688
65.8988	1.99623 E-4	7.79939 E-3	39.0705
65.9988	1.99524 E-4	7.79585 E-3	39.0723
66.0988	1.99424 E-4	7.79233 E-3	39.0741
66.1988	1.99326 E-4	7.78883 E-3	39.0759
66.2988	1.99227 E-4	7.78534 E-3	39.0777
66.3988	1.9913 E-4	7.78187 E-3	39.0794
66.4988	1.99032 E-4	7.77841 E-3	39.0812
66.5988	1.98935 E-4	7.77496 E-3	39.0829
66.6988	1.98838 E-4	7.77154 E-3	39.0847
66.7988	1.98742 E-4	7.76812 E-3	39.0864
66.8988	1.98646 E-4	7.76472 E-3	39.0882
66.9988	1.98551 E-4	7.76134 E-3	39.0899
67.0988	1.98456 E-4	7.75796 E-3	39.0916
67.1988	1.98361 E-4	7.75461 E-3	39.0933
67.2988	1.98267 E-4	7.75127 E-3	39.095
67.3988	1.98174 E-4	7.74794 E-3	39.0967
67.4988	1.9808 E-4	7.74463 E-3	39.0984
67.5988	1.97987 E-4	7.74133 E-3	39.1001

67.6988	1.97895 E-4	7.73805 E-3	39.1018
67.7988	1.97803 E-4	7.73478 E-3	39.1035
67.8988	1.97711 E-4	7.73152 E-3	39.1052
67.9988	1.9762 E-4	7.72828 E-3	39.1068
68.0988	1.97529 E-4	7.72506 E-3	39.1085
68.1988	1.97438 E-4	7.72185 E-3	39.1102
68.2988	1.97348 E-4	7.71865 E-3	39.1118
68.3988	1.97259 E-4	7.71547 E-3	39.1135
68.4988	1.97169 E-4	7.7123 E-3	39.1151
68.5988	1.9708 E-4	7.70914 E-3	39.1167
68.6988	1.96992 E-4	0.007706	39.1184
68.7988	1.96904 E-4	7.70287 E-3	39.12
68.8988	1.96816 E-4	7.69976 E-3	39.1216
68.9988	1.96729 E-4	7.69666 E-3	39.1232
69.0988	1.96642 E-4	7.69358 E-3	39.1248
69.1988	1.96555 E-4	7.6905 E-3	39.1264
69.2988	1.96469 E-4	7.68745 E-3	39.128
69.3988	1.96383 E-4	7.6844 E-3	39.1296
69.4988	1.96298 E-4	7.68137 E-3	39.1312
69.5988	1.96213 E-4	7.67836 E-3	39.1328
69.6988	1.96128 E-4	7.67535 E-3	39.1343
69.7988	1.96044 E-4	7.67237 E-3	39.1359
69.8988	1.9596 E-4	7.66939 E-3	39.1375
69.9988	1.95877 E-4	7.66643 E-3	39.139
70.0988	1.95794 E-4	7.66348 E-3	39.1406
70.1988	1.95711 E-4	7.66055 E-3	39.1421
70.2988	1.95629 E-4	7.65763 E-3	39.1437
70.3988	1.95547 E-4	7.65472 E-3	39.1452
70.4988	1.95465 E-4	7.65183 E-3	39.1467
70.5988	1.95384 E-4	7.64894 E-3	39.1483
70.6988	1.95303 E-4	7.64608 E-3	39.1498
70.7988	1.95223 E-4	7.64322 E-3	39.1513
70.8988	1.95143 E-4	7.64038 E-3	39.1528
70.9988	1.95063 E-4	7.63755 E-3	39.1543
71.0988	1.94984 E-4	7.63474 E-3	39.1558
71.1988	1.94905 E-4	7.63194 E-3	39.1573
71.2988	1.94826 E-4	7.62915 E-3	39.1588
71.3988	1.94748 E-4	7.62638 E-3	39.1603
71.4988	1.9467 E-4	7.62361 E-3	39.1617
71.5988	1.94592 E-4	7.62087 E-3	39.1632
71.6988	1.94515 E-4	7.61813 E-3	39.1647
71.7988	1.94439 E-4	7.61541 E-3	39.1661
71.8988	1.94362 E-4	7.6127 E-3	39.1676
71.9987	1.94286 E-4	0.00761	39.169
72.0987	1.9421 E-4	7.60732 E-3	39.1705
72.1987	1.94135 E-4	7.60464 E-3	39.1719
72.2987	1.9406 E-4	7.60199 E-3	39.1733
72.3987	1.93986 E-4	7.59934 E-3	39.1748
72.4987	1.93911 E-4	7.59671 E-3	39.1762
72.5987	1.93838 E-4	7.59409 E-3	39.1776
72.6987	1.93764 E-4	7.59148 E-3	39.179
72.7987	1.93691 E-4	7.58888 E-3	39.1804
72.8987	1.93618 E-4	7.5863 E-3	39.1818
72.9987	1.93546 E-4	7.58373 E-3	39.1832
73.0987	1.93473 E-4	7.58118 E-3	39.1846
73.1987	1.93402 E-4	7.57863 E-3	39.186
73.2987	1.9333 E-4	7.5761 E-3	39.1873
73.3987	1.93259 E-4	7.57358 E-3	39.1887
73.4987	1.93188 E-4	7.57107 E-3	39.1901
73.5987	1.93119 E-4	7.56858 E-3	39.1915

73.6987	1.93048 E-4	7.5661 E-3	39.1928
73.7987	1.92978 E-4	7.56363 E-3	39.1942
73.8987	1.92909 E-4	7.56117 E-3	39.1955
73.9987	1.9284 E-4	7.55872 E-3	39.1968
74.0987	1.92771 E-4	7.55629 E-3	39.1982
74.1987	1.92703 E-4	7.55387 E-3	39.1995
74.2987	1.92635 E-4	7.55146 E-3	39.2008
74.3987	1.92568 E-4	7.54906 E-3	39.2022
74.4987	1.925 E-4	7.54668 E-3	39.2035
74.5987	1.92433 E-4	7.54431 E-3	39.2048
74.6987	1.92367 E-4	7.54195 E-3	39.2061
74.7987	1.923 E-4	7.5396 E-3	39.2074
74.8987	1.92235 E-4	7.53726 E-3	39.2087
74.9987	1.92169 E-4	7.53494 E-3	39.21
75.0987	1.92104 E-4	7.53263 E-3	39.2113
75.1987	1.92039 E-4	7.53033 E-3	39.2125
75.2987	1.91974 E-4	7.52804 E-3	39.2138
75.3987	1.9191 E-4	7.52576 E-3	39.2151
75.4987	1.91846 E-4	7.5235 E-3	39.2163
75.5987	1.91782 E-4	7.52125 E-3	39.2176
75.6987	1.91719 E-4	0.007519	39.2188
75.7987	1.91656 E-4	7.51678 E-3	39.2201
75.8987	1.91594 E-4	7.51456 E-3	39.2213
75.9987	1.91531 E-4	7.51235 E-3	39.2226
76.0987	1.91469 E-4	7.51016 E-3	39.2238
76.1987	1.91408 E-4	7.50798 E-3	39.225
76.2987	1.91346 E-4	7.50581 E-3	39.2263
76.3987	1.91285 E-4	7.50365 E-3	39.2275
76.4987	1.91225 E-4	7.5015 E-3	39.2287
76.5987	1.91164 E-4	7.49936 E-3	39.2299
76.6987	1.91104 E-4	7.49724 E-3	39.2311
76.7987	1.91045 E-4	7.49513 E-3	39.2323
76.8987	1.90985 E-4	7.49302 E-3	39.2335
76.9987	1.90926 E-4	7.49093 E-3	39.2347
77.0987	1.90868 E-4	7.48886 E-3	39.2359
77.1987	1.90809 E-4	7.48679 E-3	39.237
77.2987	1.90751 E-4	7.48473 E-3	39.2382
77.3987	1.90693 E-4	7.48269 E-3	39.2394
77.4987	1.90636 E-4	7.48065 E-3	39.2405
77.5987	1.90579 E-4	7.47863 E-3	39.2417
77.6987	1.90522 E-4	7.47662 E-3	39.2428
77.7987	1.90465 E-4	7.47462 E-3	39.244
77.8987	1.90409 E-4	7.47263 E-3	39.2451
77.9987	1.90353 E-4	7.47066 E-3	39.2463
78.0987	1.90298 E-4	7.46869 E-3	39.2474
78.1987	1.90242 E-4	7.46674 E-3	39.2485
78.2987	1.90187 E-4	7.46479 E-3	39.2497
78.3987	1.90133 E-4	7.46286 E-3	39.2508
78.4986	1.90078 E-4	7.46094 E-3	39.2519
78.5986	1.90024 E-4	7.45903 E-3	39.253
78.6986	1.89971 E-4	7.45713 E-3	39.2541
78.7986	1.89917 E-4	7.45524 E-3	39.2552
78.8986	1.89864 E-4	7.45336 E-3	39.2563
78.9986	1.89811 E-4	7.45149 E-3	39.2574
79.0986	1.89759 E-4	7.44964 E-3	39.2585
79.1986	1.89707 E-4	7.44779 E-3	39.2595
79.2986	1.89655 E-4	7.44596 E-3	39.2606
79.3986	1.89603 E-4	7.44414 E-3	39.2617
79.4986	1.89552 E-4	7.44232 E-3	39.2628
79.5986	1.89501 E-4	7.44052 E-3	39.2638

79.6986	1.8945 E-4	7.43873 E-3	39.2649
79.7986	1.894 E-4	7.43695 E-3	39.2659
79.8986	1.89349 E-4	7.43518 E-3	39.267

APPENDIX B

	δ^{15}No/oo	REFERENCE
MINERALS		
Pitchblende, Great Bear Lake, Canada	- 7.2	78
Pitchblende, Great Bear Lake, Canada	+ 0.3	78
Pitchblende, Great Bear Lake, Canada	- 2.3	76,82
Samarkite, Mitchell Co., N.C. U.S.A.	- 4.3	78
Monzanite Sand	+ 8.3	78
Cordierite, Fort Victoria, Ndanga Dist., Africa	+ 4.3	78
Cordierite granulite, Geel-Kip, Orange River, S. Africa	+ 5.9	78
Microchine, Keystone, S. Dakota, U.S.A.	+ 9.3	78
Orthoclase, Fort Bayard, New Mexico, U.S.A.	- 1.0	78
Orthoclase, Fort Bayard, New Mexico, U.S.A.	+ 1.5	78
Biotite Deep Creek, N.C., U.S.A.	- 0.05	78
Biotite, Deep Creek, N.C., U.S.A.	+ 3.5	78
Biotite, Deep Creek, N.C., U.S.A.	+ 2.1	78
ROCKS		
Granite, Chelmsford, Mass., U.S.A.	- 0.2	76,82
Granite, Milford, Mass., U.S.A.	- 0.9	76
Granite, Zehren u Meissen, Germany	+ 8.0	79
Granite, Zehren u Meissen, Germany	+ 8.1	79
Granite, Graniteville, Mo., U.S.A.	+11.0	78
Rhyolite porphyry, Iron Mountain Mo., U.S.A.	+ 4.5	78
Rhyolite prophyry, Iron Mountain Mo., U.S.A.	+ 5.0	78
Rhyolite, Lipari, Italy	-15.6	79
Obsidian, Monolake, Calif, U.S.A.	+30.9	79
Obsidian, Lake Co., Oreg., U.S.A.	+ 1.7	78
Obsidian, Lake Co., Oreg., U.S.A.	+ 1.7	78
Andesite, Hoosac Mountain, Eureka Co., Nev., U.S.A.	-11.8	79
Andesite, San Juan Co., Colo., U.S.A.	+ 3.2	78
Andesite, San Juan Co., Colo., U.S.A.	+ 2.5	78
Trachyte, Manna Hualar, Hawaii, U.S.A.	- 1.2	79
Olivine basalt porphyry, Boulder Co., Colo., U.S.A.	+ 2.3	78
Olivine basalt porphyry, Boulder Co., Colo., U.S.A.	+ 5.8	78
Olivine basalt porphyry, Boulder Co., Colo., U.S.A.	+ 2.3	78
Amygdaloidal basalt, Keewenaw, Mich., U.S.A.	+ 5.7	78
Basalt, Disko Island, Greenland	+ 7.6	78
Basalt, Disko Island, Greenland	- 0.2	79
Basalt, Holyoke, Mass., U.S.A.	+ 4.8	79
Basalt, Holyoke, Mass., U.S.A.	+ 5.2	79
Olivine basalt, Mauna Loa, Hawaii, U.S.A.	+ 9.9	79
Dunite, Jackson Co., N.C., U.S.A.	+ 5.5	79
Dunite, Jackson Co., N.C., U.S.A.	- 1.9	78
Dunite, Jackson Co., N.C., U.S.A.	+ 4.6	78
Pyroxenite, Webster, N.C., U.S.A.	+ 2.4	78
Pyroxenite, Webster, N.C., U.S.A.	+ 2.4	78
VOLCANIC SUBLIMATES		
Sal ammoniac, Paracutin, Mexico	+13.0	76,82
Sal ammoniac, Laua, Mt. Vesuvius, Italy. 1886	+11.5	81
Sal ammoniac, Mt Etna, Sicily. 1886	+11.0	81

	δ^{15}No/oo	REFERENCE
NITRATE SEDIMENTS		
Nitrate, Tarapaca, Chile	- 2.6	76,82
Caliche blanco, To opilla, Chile	- 2.3	81
Caliche blanco, Tocopilla, Chile	- 5.0	81
Caliche Colorado, Tocopilla, Chile	- 1.2	81
Caliche Colorado, Tocopilla, Chile	- 5.4	81
Soil. Lake Yamanaka	4.6	86
Soil. Tokyo	6.4	86
NATURAL GAS, OIL AND COAL		
Natural gas (82% CH_4 15% N_2) Slochteren borehole, Neth.	+18	83
Mine Gas (98% CH_4 1% N_2) State mine, Emma, S Limburg, Netherlands	+12	83
Coal, State Mine, Maurits, South Limburg, Neth.	+ 2	83
Natural gas, Ella Well	- 8.1	76,82
Natural gas, Plaisted No 1 Well, Marchand Formation Okla., U.S.A.	- 3.5	76,82
Natural gas. Fletcher No 10 Well. Marchand formation	- 7.6	76,82
Petroleum, Fletcher No 10 Well. Marchand formation	+ 3.8	76,82
Natural gas Steve No 1 Well. Upper Bradley formation, Okla., U.S.A.	- 8.2	76,82
Petroleum, Steve No 1 Well. Upper Bradley formation, Okla., U.S.A.	+ 4.3	76,82
Natural gas Steve No 1 Well. Lower Bradley formation, Okla., U.S.A.	+ 2.9	76,82
Natural gas. Bitt No 1 Well, Hart formation. Okla., U.S.A.	-11.5	76,82
Natural gas. Washington Co., Ark., U.S.A.	- 5.9	76,82
Natural gas. Sylamore formation, Washington Co., Ark., U.S.A.	+ 2.7	84
Oil, Nedrano Well No 13, Medrano formation, Okla., U.S.A.	+ 3.5	76,82
Oil, Garrison No 3 Well, Rave formation, Okla., U.S.A.	+ 5.2	76,82
Oil, Shim No 5 Well, Bartlesvilles formation, Okla., U.S.A.	+ 6.3	76,82
Oil, Sells Sands formation, Franklin Co., Ark., U.S.A.	$\bar{X}$+82	84
Oil, Sarukawa, Akita Prefecture 1	+ 5.1	72
2	+ 4.9	72
3	+ 3.1	72
4	+ 2.3	72
Oil, Barato, Mokkaido 1	+ 3.6	72
2	+ 4.6	72
Oil brine, Sarukawa, Akika Prefecture	+ 1.1	72
Oil brine, Barato, Mokkaido	+ 3.4	72
Oil brine, Zeigo, Niigata Prefecture	+ 4.1	72
Peat Eire	+ 1.9	76,82
Peat Junius, N.Y., U.S.A.	- 2.8	76,82
Liquite Coal, Bowman, N.O., U.S.A.	- 1.2	76,82
Bitaminous coal, Pittsburgh Pa., U.S.A.	- 0.9	76,82
Cannel Coal, Cannel City, Ky., U.S.A.	+ 1.6	76,82
Anthracite Coal, Gunnison, Colo., U.S.A.	- 1.2	76,82
Anthracite Coal, Lehigh Pa., U.S.A.	- 1.4	76,82
Wealden Coal, Northern Germany	$\bar{X}$+ 2.8	81
Carboniferous Coal, N.W. Germany	$\bar{X}$-10	81

	$D^{15}No/oo$	REFERENCE
ORGANIC MATERIAL		
Weeds, local	+ 4.3	76,82
Oats, unknown origin	+ 6.2	76,82
Dandelion local	- 2.8	76,82
White clover leaves, local	- 6.5	76,82
Red oak leaves, local	- 0.9	76,82
Cedar leaves, local	+ 1.3	76,82
American elm leaves, local	+ 1.9	76,82
Chicken egg, local	+ 5.8	76,82
Clam flesh, Atlantic Ocean	+ 7.3	76,82
Lamb flesh, unknown origin	+ 5.0	76,82
Milk, local	+ 5.1	76,82
White rate, local: range: +0.3 to 12.1	+ 6.8	76,82
Fir, Piceas abies, Ekolsund, Sweden	- 3.8	81
Birch, Betula alba, Ekoslund, Sweden	- 2.2	81
Seaweed, Tokyo Bay, Japan	+ 8.1	76,82
Marine Algae	$\bar{X}$+ 7.5	86
Fish	+15.9	86
Plankton, Marine	+ 7.5	86
Miscanthus siensis	- 1.0	92
Wild rose	+ 2.2	72
Clover	0.0	72
Dandelion	+ 5.9	72
Chickweed	+ 5.9	72
Fern	- 0.6	72
Moss	- 0.4	72
Pine	+ 1.1	72
Sim tree	+ 2.7	72
Cryptomeria	+ 1.0	72
Pig	+ 7.6	72
Milk	+ 7.7	72
Egg White	+ 8.8	72
Egg Yolk	+ 7.0	72
WATER		
River Tone, Japan	+ 8.6	72
River Yodo, Japan	+ 7.6	72
River Asahi, Japan	$\bar{X}$+ 8.9	72
River Yashino, Japan	+ 1.9	72
Rain Tokyo, NH_4	- 9.7	72
Rain Tokyo, NO_3	+ 4.3	72
Rain Tokyo, NH_4	- 8.3	72
Rain NO_3	- 3.2	72
Rain NH_3	+ 5.1	85

APPENDIX C

BASIC PROGRAMMES

1. GASAN

2. WATCAL

3. AIRCAL

4. N_2/Ar

5. MCCLEOD

1. GASAN

```
READY.

 90 :REM TRACER CALIB OF 10/12 SEPT 80
100 DIM G$(6),E$(8),R(6),M(6),X(4,6),V(3,6),S(3,6)
110 PRINT"ANALYSIS OF DISSOLVED GASES IN WATER"
120 PRINT "ENTER SAMPLE NAME WITH GRID REFERENCE"
130 INPUT N$
140 PRINT"ENTER COLLECTION DATE AND ANALYSISDATE"
150 INPUT D1$,D2$
160 PRINT "ENTER COLLECTION TEMPERATURE OF SAMPLE"
170 INPUT T
180 PRINT"WHICH TRACER SPIKE WAS USED?"
190 INPUT Y
200 PRINT "SEQUENTIAL NO. OF TRACER SPIKE SINCE CALIB.?"
210 INPUT Y1
220 PRINT"ENTER LOWER KEY NO. OF SAMPLE TUBE USED"
230 INPUT N
240 FOR I=1 TO6
250 READ E$ (I) :REM ISOTOPE RATIOS DETERMINED
260 DATA "  3HE &  4HE"," 20NE &  22NE","  38AR &  40AR","  84KR &  86KR"
270 DATA "124XE & 132XE","  28N &  30N"
280 PRINT"ENTER     ";E$(I);"  ION CURRENTS"
290 INPUT G(I),H(I)
300 IF G(I)=0 GOTO 340
310 IF H(I)=0 GOTO 340
320 R(I)=G(I)/H(I)
330 IF G(I)<0 GOTO 350
340 R(I)=0
350 NEXT I
360 FOR I=1 TO 6
390 READ G$(I)
400 NEXT I
410 DATA "HE*1E8","NE*1E7","AR*1E4","KR*1E3","XE*1E3","N2*1E3"
420 GOSUB 980
430 FOR I=1 TO 6 :REM CALC OF GAS CONTENTS
440 IF R(I)=0 GOTO480
450 V(2,I)=S(Y,I):REM S READ IN FROM SUBR.
460 V(1,I)=V(2,I)*(X(1,I)-X(2,I)*R(I))/(X(4,I)*R(I)-X(3,I))
470 V(1,I)=V(1,I)/W :REM VOL GAS L/CM3 WATER
480 NEXTI
490 IF R(6) =0 GOTO  510
500 R9=V(1,6)/V(1,3)
510 FOR I=1 TO 6
520 IF R(I)=0 GOTO540
530 V(3,I)=V(1,I)
```

```
540 NEXT I
550 IF V(1,2)<=2.2E-7 GOTO640
560 J=V(1,2)-2.2E-7 :REM FOR T=5 MORR& JOHN
570 FOR I=1 TO6
580 IF R(I)=0 GOTO 600
590 V(3,I)=V(1,I)-J*M(I)/M(2)
600 NEXT
610 V(1,1)=V(1,1)*1E8:V(1,2)=V(1,2)*1E7:V(1,3)=V(1,3)*1E4:V(1,4)=V(1,4)*1E8
620 V(1,5)=V(1,5)*1E8:V(1,6)=V(1,6)*1E2
625 V(3,1)=V(3,1)*1E8:V(3,2)=V(3,2)*1E7:V(3,3)=V(3,3)*1E4:V(3,4)=V(3,4)*1E8
630 V(3,5)=V(3,5)*1E8:V(3,6)=V(3,6)*1E2
635 S(1,1)=S(1,1)*1E8:S(1,2)=S(1,2)*1E7:S(1,3)=S(1,3)*1E4:S(1,4)=S(1,4)*1E8
636 S(1,5)=S(1,5)*1E8:S(1,6)=S(1,6)*1E2
640 Z=Z+1
645 OPEN1,4:CMD1
650 PRINT#1
660 PRINT#1
670 PRINT#1
680 PRINT#1,CHR$(1)"□H@NALYSIS OF □D@ISSOLVED □G@ASES IN □W@ATER"
690 PRINT#1
700 PRINT#1,"SAMPLE NAME:    ";N$
710 PRINT#1,"SAMPLE COLLECTION TEMP.=  ";T;"   DEG.CENT."
720 PRINT#1,"COLLECTED ON   ";D1$ ;"  ANALYSED ON  ";D2$
730 PRINT#1
740 PRINT#1,"VOLUME OF SAMPLE TUBE  ";N;"=";W;"  CM3"
750 PRINT#1,"TRACER NUMBER  ";Y;"  SEQUENTIAL NUMBER  ";Y1
760 PRINT#1
770 PRINT#1, "GAS CONTENTS OF SAMPLE":PRINT#1
780 PRINT#1,"GAS       IC.LIGHT  IC.HEAVY          CONC.              CORR.CONC."
785 OPEN2,4,1:OPEN3,4,2
787 PRINT#3,"AAAAAA   999.999   999.999        999999.999         999999.999"
790 FOR I=1 TO 6
800 IF R(I) =0 GOTO 820
810 PRINT#2,G$(I);CHR$(29);G(I);H(I);V(1,I);V(3,I)
820 NEXT I
825 PRINT#3:CLOSE3:PRINT#2:CLOSE2
830 IF R(6) =0 GOTO 860
840 PRINT#1
850 PRINT#1,"NITROGEN/ARGON RATIO =  ";R9
860 PRINT#1
870 PRINT#1
880 PRINT#1,"TRACER CALIB. OF  ";T$;"% SEQUENTIAL FACTOR =  ";S9
890 PRINT#1
900 PRINT#1,"GAS            M.F.LIGHT     M.F.HEAVY          VOLUME CM3"
905 OPEN2,4,1:OPEN4,4,2
907 PRINT#4,"AAAAAA           9.999          9.999           9999.999"
910 FOR I=1 TO 6
920 PRINT#2,G$(I);CHR$(29);X(1,I);X(2,I);S(1,I)
930 NEXTI
935 PRINT#4:CLOSE4:PRINT#2:CLOSE2
940 PRINT#1
950 PRINT#1
955 PRINT#1:CLOSE1
960 IFZ<3 GOTO 640
970 STOP
980 FOR I=1 TO6 :REM READS MOL FRACTS CH3 AND ISOTOPES IN ATM
990 READ M(I),X(3,I),X(4,I)
1000 NEXT I
1010 DATA 5.2E-6,1.3E-6,0.999992
1020 DATA 1.81E-5,0.9105,0.0894
1030 DATA 9.5CE-3,0.0006,0.996
1040 DATA 1.14E-6,0.569,0.1737
1050 DATA 8.06E-8,9.6E-4,0.2689
1060 DATA 0.7803,0.9963,0.0037
1070 FOR I=1 TO6 :REM READS MOL FRACTS ISOTOPES IN TRACER
1080 READ X(1,I),X(2,I)
1090 NEXT I :REM MOL FRACTS LIGHT AND HEAVY GASES IN TRACER
1100 DATA 0.89,0.11,0.124,0.876,0.34,0.66,0.02,0.98
1110 DATA 0.207,0.01,0.375,0.625
1120 Y2=Y1-1
1130 S9=0.9989641^Y2 :REM SPIKE CORR. FACTOR
1140 FOR I=1 TO
```

```
1150 READ S(1,I) :REM READS TRACER CALIB.
1160 S(1,I)=S(1,I)*S9
1170 S(2,I)=0.996872*S(1,I) :REM CALCS TRACER 2
1180 S(3,I)=0.975412*S(1,I) :REM CALC TRACER 3
1190 NEXT I
1200 DATA 6.040E-7,1.530E-7,2.000E-4,4.0300E-8,1.240E-8,6.320E-3
1210 T$="10/12 SEPT 80" :REM DATE OF TRACER CALIB
1220 GOSUB 2000
1230 RETURN
2000 DIM L(160),W(160)
2010 FOR I=1 TO 160
2020 READ L(I),W(I)
2030 IF L(I)=N GOTO 2050
2040 NEXT I
2050 W=W(I)
2060 DATA 1,0.939,3,1.199,5,1.227,10,1.228,11,1.215
2070 DATA 13,1.195,15,1.122,17,1.278,20,1.208,24,1.085
2080 DATA 26,1.202,28,1.211,30,1.080,32,1.127,34,1.124
2090 DATA 37,1.172,39,1.302,41,1.168,43,1.149,45,1.109
2100 DATA 47,1.257,49,1.235,51,1.189,53,1.187,55,1.107
2110 DATA 57,1.174,59,1.173,61,1.193,63,1.115,66,1.227
2120 DATA 68,1.094,70,1.293,72,1.248,74,1.185,76,1.036
2130 DATA 78,1.134,80,1.199,82,1.243,84,1.165,86,1.302
2140 DATA 90,1.150,92,1.177,94,1.151,96,1.186,98,1.149
2150 DATA 100,1.229,102,1.178,104,1.097,120 1.217,122,1.140
2160 DATA 126,1.140,128,1.228,130,1.199,132,1.157,134,1.274
2170 DATA 136,1.202,138,1.204,150,1.228,200,1.363,204,1.472
2180 DATA 202,1.2787,212,1.4405,216,1.2789,238,1.466,240,1.4279
2190 DATA 242,1.1238,248,1.7308,254,1.4251,260,1.4546,272,1.2905
2200 DATA 206,1.464,208,1.658,214,1.500,218,1.330,220,1.509
2210 DATA 222,1.340,224,1.488,226,1.613,228,1.611,230,1.288
2220 DATA 232,1.372,234,1.532,236,1.300,244,1.402,246,1.253
2230 DATA 250,1.437,252,1.492,256,1.597,258,1.523,262,1.429
2240 DATA 270,1.578,276,1.511,278,1.463,282,1.582,284,1.623
2250 DATA 274,1.3870,280,1.5915
2260 DATA 300,1.313,302,1.422,303,1.528,306,1.403,308,1.450
2270 DATA 309,1.505,313,1.443,315,1.382,316,1.378,317,1.396
2280 DATA 319,1.396,322,1.324,324,1.440,325,1.448,327,1.399
2290 DATA 328,1.473,329,1.357,341,1.439,344,1.305,345,1.478
2300 DATA 352,1.522,356,1.381,314,1.4559,323,1.4332,340,1.4688
2310 DATA 350,1.3509,353,1.4837,354,1.4940,355,1.5418
2320 DATA 357,1.3096,260,1.4566,318,1.4105,246,1.2638
2330 DATA 348,1.3382,342,1.4955,208,1.6605,163,1.1068
2340 DATA 349,1.5099,307,1.3916,311,1.5245,343,1.4117
2350 DATA 347,1.4183,346,1.3798,305,1.4033,500,1.00
2360 RETURN
2370 END
READY.
```

2. WATCAL

```
READY.

100 DIM G$(6),E$(6),R(6),M(6),X(4,6),V(2,6),S(3,6)
110 PRINT "TRACER CALIBRATION WITH AIR SATURATED WATER. ENTER DATE"
120 INPUT D$
130 PRINT "ATMOSPHERRIC PRESSURE ,MM.HG AND TEMPERATURE, C"
140 INPUT P1,T
150 IF T<5 GOTO 200 IF T>30 GOTO 200
170 IF P1<700 GOTO 200
180 IF P1>800 GOTO 200
190 GOTO 220
200 PRINT"ERROR IN P OR T . REPEAT ENTRIES"
210 GOTO 140
220 PRINT"ENTER THE LOWER KEY NUMBER OF SAMPLE TUBE USED"
230 INPUT N
240 PRINT"WHICH TRACER WAS USED ? ANSWER 1,2 OR 3"
250 INPUT S
```

```
260 FOR I= 1 TO6
270 READ E$(I):REM ISOTOPE RATIOS DETERMINED
280 DATA "3HE & 4HE     ","20NE & 22NE   ","38AR & 40AR   ","84KR & 86KR   "
290 DATA "124XE & 132XE","28N & 30N     "
300 PRINT"ENTER    ";E$(I);"    ION CURRENTS"
310 INPUT G1,G2
320 IF G1=0 GOTO 360
330 IF G2=0 GOTO 360
340 R(I) =G1/G2
350 IF G1<>0 GOTO370
360 LET R(I)=0
370 NEXT I
400 FOR I=1 TO6
410 READ G$(I)
420 NEXT I
430 DATA "HE*1E8","NE*1E7","AR*1E4","KR*1E8","XE*1E9","N2*1E3"
440 T=T+273.18
450 P2=21.0109-5321.01/T :REM V.P. WATER AT T
460 P2=EXP(P2)
470 P=P1-P2 :REM CORR ATM PRESS,SAT.WATER VAPOUR
480 GOSUB 1090
490 FOR I=1 TO 6
500 IF R(I)=0 GOTO 540
510 V(1,I)=K(I) :REM VOL GAS I IN THE WATER
520 V(2,I)=V(1,I)*(X(4,I)*R(I)-X(3,I))/(X(1,I)-X(2,I)*R(I))
530 S(Y,I)=V(2,I) :REM VOL GAS I IN TRACER Y
540 NEXT I
550 IF Y=2 GOTO 620
560 IF Y=3 GOTO670
570 FOR I= 1TO 6
580 S(2,I)=0.996872*S(1,I)
590 S(3,I)=0.975412*S(1,I)
600 NEXT I
610 GOTO 710
620 FOR I = 1 TO6
630 S(1,I) =1.00314*S(2,I)
640 S(3,I)=0.978472*S(2,I)
650 NEXT I
660 GOTO 710
670 FOR I= 1 TO 6
680 S(1,I)=1.02521*S(3,I)
690 S(2,I)=1.02200*S(3,I)
700 NEXT I
710 FOR I = 1TO 3
720 S(I,1)=S(I,1)*1E8:S(I,2)=S(I,2)*1E7:S(I,3)=S(I,3)*1E4
730 S(I,4)=S(I,4)*1E8:S(I,5)=S(I,5)*1E9:S(I,6)=S(I,6)*1E3
735 NEXT I
740 Z=Z+1
745 OPEN1,4:CMD1
750 PRINT#1
760 PRINT#1
770 PRINT#1
780 PRINT#1,CHR$(1)"TRACER CALIB. WITH AIR SAT. WATER ON    ";D$
790 PRINT#1
800 PRINT#1,TAB(14);"TRACER 1       TRACER 2       TRACER 3"
805 PRINT#1:OPEN2,4,1:OPEN3,4,2
810 PRINT#1
815 PRINT#3,"AAAAAA        999.9999        999.9999        999.9999"
820 FOR I=1 TO 6
830 IF R(I) =0 GOTO 850
840 PRINT#2,G$(I);CHR$(29);S(1,I);S(2,I);S(3,I)
850 NEXT I
855 PRINT#3:CLOSE3
860 PRINT#1
870 PRINT#1
880 PRINT#1,"BASED ON CALIBRATION OF TRACER"  ;Y
890 PRINT#1,"VOLUME OF SAMPLE TUBE  ";N;" = ";W;"  CM3"
900 PRINT#1
910 PRINT#1,"ATM. PRESS. =  ";P1; "WATER VAP PRESS. AT T = ";P2;"MM HG"
920 PRINT#1,"ROOM TEMPERATURE =  ";T;" K"
930 PRINT#1
940 PRINT#1
```

```
950 PRINT#1,"MOLE FRACTION OF ISOTOPES IN TRACER"
960 PRINT#1,"GAS";TAB(15);"MF LIGHT ISOTOPE"TAB(8);"MF HEAVY ISOTOPE"
965 OPEN3,4,2
968 PRINT#3,"AAAAAAAAAAAAA       9.999                          9.999"
970 FOR I= 1 TO6
980 PRINT#2,E$(I);CHR$(29);X(1,I);X(2,I)
990 NEXT I
995 PRINT#3:CLOSE3
1000 PRINT#1
1010 PRINT#1
1020 PRINT#1,"MEASURED ISOTOPE RATIOS FOR MIXTURE OF GASES"
1030 OPEN3,4,2
1035 PRINT#3,"AAAAAAAAAAAAA                 999.999999"
1040 FOR I=1 TO6
1050 PRINT#2,E$(I);CHR$(29);R(I)
1060 NEXT I
1062 PRINT#3:CLOSE3:PRINT#2:CLOSE2
1065 PRINT#1:CLOSE1
1070 IF Z<2 GOTO 740
1080 STOP
1090 FOR I= 1TO 6
1100 READ M(I),X(3,I),X(4,I)
1110 NEXT I
1120 DATA 5.2E-6,1.3E-6,0.999999
1130 DATA 1.81E-5,0.9105,0.0894
1140 DATA 9.56E-3,0.0006,0.996
1150 DATA 1.14E-6,0.569,0.1737
1160 DATA 8.06E-8,9.6E-4,0.2689
1170 DATA 0.7803,0.9963,0.0037
1180 FOR I=1TO 6 :REM READS MOL FRACTS ISOTOPES IN TRACER
1190 READ X(1,I),X(2,I)
1200 NEXT I :REM MOL FRACTS LIGHT AND HEAVY GASES IN TRACER
1210 DATA .79 ,0.21,0.133,0.867,0.305,.695,.02,0.98
1220 DATA 0.207,0.01,0.375,0.625
1230 FOR I = 1TO 6
1250 READ H(I),J(I)
1260 NEXT I
1270 GOSUB 2000
1280 FOR I =1 TO 5
1290 K(I)=0
1300 K(I)=20.5*LOG(T)
1310 K(I) =K(I)+J(I)/T
1320 K(I)=K(I)-H(I)
1330 K(I)=EXP(K(I))
1340 K(I)=K(I)*W/1000 :REM CM3/G AT 1ATM OF GAS I
1350 K(I)=K(I)*M(I)*P/760 :REM  CM3/G AT PP OF GAS I IN AIR
1360 NEXT I
1370 LET K(6)=0
1380 LET K(6)=24.3696*LOG(T)
1390 K(6)=K(6)+J(6)/T-H(6)
1400 DATA 135.823,6309.08 :REM HE MORRISON AND JOHNSTON 1954
1410 DATA 136.801,6654.47 :REM NE
1420 DATA 138.781,7575.51 :REM AR
1430 DATA 139.154,7851.82 :REM KR
1440 DATA 140.080,8300.82 :REM XE
1450 DATA 171.854,8576.61 :REM N2 WEISS
1460 LET K(6)=EXP(K(6))
1470 K(6)=K(6)*W*M(6)*P/760
1480 RETURN
2000 DIM L(160),W(160)
2010 FOR I=1 TO160
2020 READ L(I),W(I)
2030 IF L(I) =N GOTO 2050
2040 NEXT I
2050 W=W(I)
2060 DATA1,0.939,3,1.199,5,1.227,10,1.228,11,1.215
2070 DATA 13,1.195,15,1.122,17,1.278,20,1.208,24,1.085
2080 DATA 26,1.202,28,1.211,30,1.080,32,1.127,34,1.124
2090 DATA 37,1.172,39,1.302,41,1.168,43,1.149,45,1.109
2100 DATA 47,1.257,49,1.235,51,1.189,53,1.187,55,1.107
2110 DATA 57,1.174,59,1.173,61,1.193,63,1.115,66,1.227
2120 DATA 68,1.094,70,1.293,72,1.248,74,1.185,76,1.036
```

```
2130 DATA 78,1.134,80,1.199,82,1.243,84,1.165,86,1.302
2140 DATA 90,1.150,92,1.177,94,1.151,96,1.186,98,1.149
2150 DATA 100,1.229,102,1.178,104,1.097,120,1.217,122,1.148
2160 DATA 126,1.140,128,1.228,130,1.199,132,1.157,134,1.274
2170 DATA 136,1.202,138,1.204,150,1.223,200,1.363,204,1.472
2180 DATA 202,1.2787,212,1.4405,216,1.2789,238,1.466,240,1.4279
2190 DATA 242,1.1238,248,1.7308,254,1.4251,260,1.4546,272,1.2965
2200 DATA 206,1.464,208,1.658,214,1.500,218,1.330,220,1.509
2210 DATA 222,1.340,224,1.488,226,1.613,228,1.611,230,1.288
2220 DATA 232,1.372,234,1.532,236,1.330,244,1.402,246,1.253
2230 DATA 250,1.437,252,1.492,256,1.597,258,1.523,262,1.429
2240 DATA 270,1.578,276,1.511,2.78,1.463,282,1.592,284,1.623
2250 DATA 274,1.3870,280,1.5915
2260 DATA 300,1.313,302,1.422,303,1.528,306,1.403,308,1.45
2270 DATA 309,1.505,313,1.443,315,1.302,316,1.370,317,1.396
2280 DATA 319,1.396,322,1.324,324,1.440,325,1.448,327,1.309
2290 DATA 328,1.473,329,1.357,341,1.439,344,1.385,345,1.478
2300 DATA 352,1.522,356,1.381,314,1.4559,323,1.4332,340,1.4688
2310 DATA 350,1.3509,353,1.4337,354,1.4940,355,1.5418
2320 DATA 357,1.3096,260,1.4566,318,1.4105,246,1.2638
2330 DATA 348,1.3382,342,1.4955,208,1.6605,163,1.1068
2340 DATA 349,1.5099,307,1.3916,311,1.5245,343,1.4117
2350 DATA 347,1.4183,346,1.3798,305,1.4033,3400,4.094
2360 RETURN
2370 END
READY.


WATCAL

READY.

 100 DIM G$(6),E$(6),R(6),M(6),X(4,6),V(2,6),S(3,6)
 110 PRINT "TRACER CALIBRATION WITH AIR SATURATED WATER. ENTER DATE"
 120 INPUT D$
 130 PRINT "ATMOSPHERRIC PRESSURE ,MM.HG AND TEMPERATURE, C"
 140 INPUT P1,T
 150 IF T<5 GOTO 200 IF T>30 GOTO 200
 170 IF P1<700 GOTO 200
 180 IF P1>800 GOTO200
 190 GOTO 220
 200 PRINT"ERROR IN P OR T . REPEAT ENTRIES"
 210 GOTO 140
 220 PRINT"ENTER THE LOWER KEY NUMBER OF SAMPLE TUBE USED"
 230 INPUT N
 240 PRINT"WHICH TRACER WAS USED ? ANSWER 1,2 OR 3"
 250 INPUT Y
 260 FOR I= 1 TO6
 270 READ E$(I):REM ISOTOPE RATIOS DETERMINED
 280 DATA "3HE & 4HE","20NE & 22NE","38AR & 40AR","84KR & 86KR"
 290 DATA   "124XE & 132XE","28N & 30N"
 300 PRINT"ENTER   ";E$(I);"   ION CURRENTS"
 310 INPUT G1,G2
 320 IF G1=0 GOTO 360
 330 IF G2=0 GOTO 360
 340 R(I) =G1/G2
 350 IF G1<>0 GOTO370
 360 LET R(I)=0
 370 NEXT I
 400 FOR I=1 TO6
 410 READ G$(I)
 420 NEXT I
 430 DATA "HE","NE","AR","KR","XE","N2"
 440 T=T+273.18
 450 P2=21.0109-5321.01/T :REM V.P. WATER AT T
 460 P2=EXP(P2)
 470 P=P1-P2 :REM CORR ATM PRESS,SAT.WATER VAPOUR
 480 GOSUB 1090
 490 FOR I=1 TO 6
 500 IF R(I)=0 GOTO 540
 510 V(1,I)=R(I) :REM VOL GAS I IN THE WATER
```

```
520 V(2,I)=V(1,I)*(X(4,I)*R(I)+X(3,I))/(X(3,I)+X(4,I)*R(I))
530 S(Y,I)=V(2,I) :REM VOL GAS I IN TRACER Y
540 NEXT I
550 IF Y=2 GOTO 620
560 IF Y=3 GOTO670
570 FOR I= 1TO 6
580 S(2,I)=0.996872*S(1,I)
590 S(3,I)=0.975412*S(1,I)
600 NEXT I
610 GOTO 740
620 FOR I = 1 TO6
630 S(1,I) =1.00314*S(2,I)
640 S(3,I)=0.978472*S(2,I)
650 NEXT I
660 GOTO 740
670 FOR I= 1 TO 6
680 S(1,I)=1.02521*S(3,I)
690 S(2,I)=1.02200*S(3,I)
700 NEXT I
740 Z=Z+1
745 OPEN1,4:CMD1
750 PRINT#1
760 PRINT#1
770 PRINT#1
780 PRINT#1,CHR$(1)"TRACER CALIB. WITH AIR SAT. WATER ON    ";D$
790 PRINT#1
800 PRINT#1,TAB(10);"TRACER 1";TAB(10);"TRACER 2";TAB(10);"TRACER3"
810 PRINT#1
820 FOR I=1 TO 6
830 IF R(I) =0 GOTO 850
840 PRINT#1,G$(I);TAB(10);S(1,I);TAB(10);S(2,I);T AB(10);S(3,I)
850 NEXT I
860 PRINT#1
870 PRINT#1
880 PRINT#1,"BASED ON CALIBRATION OF TRACER"  ;Y
890 PRINT#1,"VOLUME OF SAMPLE TUBE  ";N;" = ";W;"  CM3"
900 PRINT#1
910 PRINT#1,"ATM. PRESS. =  ";P1; "WATER VAP PRESS. AT T = ";P2;"MM HG"
920 PRINT#1,"ROOM TEMPERATURE =  ";T;" K"
930 PRINT#1
940 PRINT#1
950 PRINT#1,"MOLE FRACTION OF ISOTOPES IN TRACER"
960 PRINT#1,"GAS";TAB(15);"MF LIGHT";TAB(15);"MF HEAVY ISOTOPE"
970 FOR I= 1 TO6
980 PRINT#1,E$(I); TAB(15);X(1,I);TAB(15);X(2,I)
990 NEXT I
1000 PRINT#1
1010 PRINT#1
1020 PRINT#1,"MEASURED ISOTOPE RATIOS FOR MIXTURE OF GASES"
1030 PRINT#1
1040 FOR I=1 TO6
1050 PRINT#1,E$(I);TAB(15);R(I)
1060 NEXT I
1065 PRINT#1:CLOSE1
1070 IF Z<2 GOTO 740
1080 STOP
1090 FOR I= 1TO 6
1100 READ M(I),X(3,I),X(4,I)
1110 NEXT I
1120 DATA 5.2E-6,1.3E-6,0.999999
1130 DATA 1.81E-5,0.9105,0.0894
1140 DATA 9.5E-3,0.0006,0.994
1150 DATA 1.14E-2,0.569,0.1737
1160 DATA 5.08E-6,9.8E-4,0.2689
1170 DATA 0.7803,0.9963,0.0037
1180 FOR I=1TO 6 :REM READS MOL FRACTS ISOTOPES IN TRACER
1190 READ X(1,I),X(2,I)
1200 NEXT I :REM MOL FRACTS LIGHT AND HEAVY GASES IN TRACER
1210 DATA 0.89,0.11,0.124,0.876,0.34,0.66,0.02,0.98
1220 DATA 0.207,0.01,0.375,0.625
1230 FOR I = 1TO 6
1250 READ H(I),J(I)
```

```
1260 NEXT I
1270 GOSUB 2000
1280 FOR I =1 TO 5
1290 K(I)=0
1300 K(I)=20.5*LOG(T)
1310 K(I) =K(I)+J(I)/T
1320 K(I)=K(I)-H(I)
1330 K(I)=EXP(K(I))
1340 K(I)=K(I)*W/1000 :REM CM3/G AT 1ATM OF GAS I
1350 K(I)=K(I)*M(I)*P/760 :REM  CM3/G AT PP OF GAS I IN AIR
1360 NEXT I
1370 LET K(6)=0
1380 LET K(6)=24.3696*LOG(T)
1390 K(6)=K(6)+J(6)/T-H(6)
1400 DATA 135.823,6309.08 :REM HE MORRISON AND JOHNSTON 1954
1410 DATA 136.801,6654.47 :REM NE
1420 DATA 138.781,7575.51 :REM AR
1430 DATA 139.154,7851.82 :REM KR
1440 DATA 140.080,8300.82 :REM XE
1450 DATA 171.854,8576.61 :REM N2 WEISS
1460 LET K(6)=EXP(K(6))
1470 K(6)=K(6)*W*M(6)*P/760
1480 RETURN
2000 DIM L(160),W(160)
2010 FOR I=1 TO160
2020 READ L(I),W(I)
2030 IF L(I) =N GOTO 2050
2040 NEXT I
2050 W=W(I)
2060 DATA1,0.939,3,1.199,5,1.207,10,1.228,11,1.215
2070 DATA 13,1.195,15,1.122,17,1.270,20,1.208,24,1.085
2080 DATA 26,1.202,28,1.211,30,1.080,32,1.127,34,1.124
2090 DATA 37,1.172,39,1.302,41,1.168,43,1.149,45,1.109
2100 DATA 47,1.257,49,1.205,51,1.189,53,1.187,55,1.107
2110 DATA 57,1.174,59,1.173,61,1.193,63,1.115,66,1.227
2120 DATA 68,1.094,70,1.293,72,1.248,74,1.185,76,1.036
2130 DATA 78,1.134,80,1.199,82,1.243,84,1.165,86,1.302
2140 DATA 90,1.150,92,1.177,94,1.151,96,1.186,98,1.149
2150 DATA 100,1.229,102,1.178,104,1.097,120,1.217,122,1.148
2160 DATA 126,1.140,128,1.228,130,1.199,132,1.157,134,1.274
2170 DATA 136,1.202,138,1.204,150,1.223,200,1.368,204,1.472
2180 DATA 202,1.2787,212,1.4405,216,1.2739,238,1.466,240,1.4279
2190 DATA 242,1.1238,248,1.7308,254,1.4251,260,1.4546,272,1.2905
2200 DATA 206,1.464,208,1.658,214,1.500,218,1.330,220,1.509
2210 DATA 222,1.340,224,1.488,226,1.613,228,1.611,230,1.288
2220 DATA 232,1.372,234,1.502,236,1.330,244,1.402,246,1.250
2230 DATA 250,1.437,252,1.492,256,1.597,258,1.523,262,1.429
2240 DATA 270,1.578,276,1.511,2.78,1.463,282,1.592,284,1.623
2250 DATA 274,1.3870,280,1.5915
2260 DATA 300,1.313,302,1.422,303,1.528,306,1.403,308,1.45
2270 DATA 304,1.505,312,1.443,315,1.300,316,1.370,317,1.396
2280 DATA 319,1.396,322,1.324,324,1.440,325,1.440,327,1.209
2290 DATA 328,1.473,329,1.357,341,1.439,344,1.385,345,1.478
2300 DATA 352,1.522,356,1.381,314,1.4559,323,1.4382,340,1.4688
2310 DATA 350,1.3509,353,1.4007,354,1.4940,355,1.5418
2320 DATA 357,1.3096,260,1.4560,318,1.4105,246,1.2638
2330 DATA 348,1.3382,342,1.4955,208,1.6605,163,1.1068
2340 DATA 349,1.5095,307,1.3916,311,1.5245,343,1.4117
2350 DATA 347,1.4183,346,1.3798,305,1.4033
2360 RETURN
2370 END
READY.


AIRCAL

READY.


READY.
```

3. AIRCAL

```
100 DIM N$(2),G$(6),E$(6),R(6),M(6),X(4,6),V(2,6),S(3,6)
110 N$(1)="F/(D+E+F)"
120 N$(2)="(F+G+H)/(D+E+F+G+H)"
130 PRINT"TRACER CALIBRATION WITH AIR SPIKE. ENTER DATE"
140 INPUT D$
150 PRINT "ATMOSPHERIC PRESS., MM.HG & TEMPERATURE,C"
160 INPUT P1,T
170 IF T<5 GOTO 220
180 IF T>30 GOTO 220
190 IF P1<700 GOTO 220
200 IF P1>800 GOTO220
210 GOTO 240
220 PRINT"ERROR IN P OR T. REPEAT ENTERIES"
230 GOTO 160
240 PRINT "ENTER THE RELATIVE HUMIDITY AT AIR SPIKE LOADING"
250 INPUT H
260 PRINT"SPIKE FRACTION USED? 1=" ;N$(1);"OR 2=" ;N$(2)
270 PRINT "ANSWER 1 OR2"
280 INPUT M
290 PRINT "SPIKES OF TYPES 1 AND 2 MUST NOT BE MIXED":PRINT:PRINT
300 PRINT "SEQUENTIAL NUMBER OF AIR SPIKE SINCE LOADING ?"
310 INPUT A
320 PRINT "WHICH TRACER WAS USED? ANSWER 1,2 OR 3"
330 INPUT Y
340 FOR I=1TO6
350 READ E$(I) :REM ISOTOPE RATIOS DETERMINED
360 DATA "  3HE &   4HE"," 20NE &  22NE"," 36AR &  40AR", " 84KR &  86KR"
370 DATA "124XE & 132XE","  28N &  30N"
380 PRINT "ENTER  ";E$(I);"  ION CURRENTS"
390 INPUT L(I),H(I)
400 IF L(I)=0 GOTO 440
410 IF H(I)=0 GOTO 440
420 R(I) =L(I)/H(I)
430 IF L(I)<30 GOTO 450
440 R(I)=0
450 NEXT I
460 FOR I= 1TO6
470 READ G$(I)
480 NEXT I
490 DATA "HE","NE","AR","KR","XE","N2"
500 GOSUB 1160
510 T=T+273.18
520 P2=21.0109-5321.01/T :REM V.P. WATER AT T
530 P2=EXP(P2)
540 P=P1-P2*H/100 :REM CORR. ATM PRESS
550 B=A-1
560 W=0.125124*P/T :REM VOL IN B AT STP
570 W1=0.993095*W :REM VOL IN D AT STP
580 IFM=2 GOTO 610
590 W2=0.3939*61.50391B*W1/61.89781A :REM VOL OF AIR SPIKE 1
600 IF M=1 GOTO 620
610 W2=4.4251*61.50391B*W1/65.9291A :REM VOL OF AIR SPIKE 2
620 FOR I=1 TO6
630 IF R(I)=0 GOTO 670
640 V(1,I)=W2*M(I) :REM VOL GAS I IN AIR SPIKE ADMITTED
650 V(2,I)=V(1,I)*((X(4,I)*R(I)-X(3,I))/(X(1,I)-X(2,I)*R(I))
660 S(Y,I)=V(2,I) :REM VOL GAS I IN TRACERY
670 NEXT I
680 IF Y=2 GOTO 750
690 IF Y=3 GOTO800
700 FOR I =1 TO 6
710 S(2,I)=0.996872*S(1,I)
720 S(3,I)=0.975412*S(1,I)
730 NEXTI
740 GOTO 840
750 FOR I =1TO 6
760 S(1,I)=1.00314*S(2,I)
770 S(3,I)=0.978472*S(2,I)
780 NEXT I
790 GOTO 840
800 FOR I = 1TO 6
810 S(1,I)=1.025.21*S(3,I)
```

```
820 S(2,I)=1.02200*S(3,I)
830 NEXT I
840 Z=Z+1
850 OPEN1,4:CMD 1
860 PRINT#1
870 PRINT#1, CHR$(1)"TRACER CALIB WITH AIRSPIKE,"  ;D$
880 PRINT#1
890 PRINT#1, TAB(15);"TRACER 1";TAB(15);"TRACER 2";TAB(15);"TRACER 3"
900 PRINT#1
910 FOR I=1TO6
920 IF R(I)=0 GOTO940
930 PRINT#1,G$(I);TAB(7);S(1,I);TAB(7);S(2,I);TAB(7);S(3,I)
940 NEXT I
950 PRINT#1
960 PRINT#1,  "BASED ON CALIBRATION OF TRACER"  ;Y
970 PRINT#1,"USING AIRSPIKE FRACTION   ";N$(M);"   SEQUENTIAL NO.    " ;A
980 PRINT#1
990 PRINT#1, "ATM. PRESS.=" ;P1; "WATER VAP PRESS. AT I=";P2;"MM.HG"
1000 PRINT#1, "ROOM TEMP =";T;"C   REL. HUMIDITY=  ";H;"PERCENT"
1010 PRINT#1
1020 PRINT#1:
1030 PRINT#1,  "MOLE FRACTS IN TRACER AND VOL GAS IN AIRSPIKE"
1040 PRINT#1, "GAS"; TAB(6);"MF LIGHT";TAB(5);"MF HEAVY      VOL IN AIRSPIKE"
1050 FOR I=1 TO 6
1060 PRINT#1, G$(I);TAB(6);X(1,I);TAB(6);X(2,I);TAB(6);V(1,I)
1070 NEXT I
1080 PRINT#1
1090 PRINT#1,"GAS       I.C LIGHT         I.C HEAVY       IC RATIO"
1100 FOR I=1TO6
1110 PRINT#1,G$(I),L(I),H(I),R(I)
1120 NEXT I
1130 PRINT#1:CLOSE1
1140 IF Z<2 GOTO 840
1150 STOP
1160 FOR I =1 TO 6 : REM READS MOL FRACTS GAS AND ISOTOPES IN ATM
1170 READ M(I),X(3,I),X(4,I)
1180 NEXT I
1190 DATA 5.2E-6,1.3E-6,0.99999 :REM HE
1200 DATA 1.81E-5,0.9105,0.0894 :REM NE
1210 DATA 9.56E-3,0.0006,0.996  :REM AR
1220 DATA 1.14E-6,0.569, 0.1737 :REM KR
1230 DATA 8.66E-8,9.6E-4,0.2689 :REM XE
1240 DATA 0.7803,0.9963,0.0037  :REM N2
1250 FOR I=1 TO6 :REM MOL FRACTS LIGHT AND HEAVY GASES IN TRACER
1260 READX(1,I),X(2,I)
1270 NEXT
1280 DATA .790,.210,.133,.867,.335,.665,0.02,.98
1290 DATA 0.207,0.625,0.375,0.625
1300 RETURN
1310 END
READY.
```

4. N_2/Ar

```
READY.

100 DIM X(2,2),Y(2,2)
110 X(1,1)=0.3335: Y(1,1)=0.6665;REM MOL FRACTS L/H ISOTOPES N2 IN TRACER
120 X(2,1)=0.9647: Y(2,1)=0.03528 :REM MOL FRACTS L/H ISOTOPES AR IN TRACER
130 X(1,2)=0.99634;Y(1,2)=0.00366 :REM MOL FRACTS L/H ISOTOPES N2 IN AIR
140 X(2,2)=0.00337: Y(2,2)=0.99663  :REM MOL FRACTS L/H ISOTOPES AR IN AIR
150 R5=X(1,1)/Y(1,1) :REM 28/30 IN TRACER
160 R6=X(2,1)/Y(2,1) :REM 36/40 IN TRACER
170 PRINT"NITROGEN/ARGON ANALYSIS, ENTER DATE":INPUT D1$
180 OPEN1,4,1:CMD 1
190 PRINT#1,CHR$(1)"  NITROGEN/ARGON ANALYSIS  ";D1$
200 PRINT#1
210 PRINT"TRACER CALIBRATION?":INPUT Q$
220 PRINT"DATE OF TRACER ADDITION?  ":INPUT D2$
```

```
230 PRINT"DATE OF N2 RATIO MEASUREMENT " ;INPUT D3$
240 PRINT"DATE OF AR RATIO MEASUREMENT ";INPUT D4$
250 PRINT#1,"DATE OF TRACER ADDITION          ";D2$
260 PRINT#1,"DATE OF N2 RATIO MEASUREMENT     ";D3$
270 PRINT#1,"DATE OF AR RATIO MEASUREMENT     ";D4$:PRINT#1:PRINT#1
280 IF Q$="NO" GOTO 600
290 PRINT#1,CHR$(1) "     TRACER CALIBRATION    ":PRINT#1
300 PRINT"ATMOSPHERIC PRESSURE ,MM HG?":INPUT P1
310 PRINT"TEMPERATURE, °C?": INPUT T
320 PRINT"WEIGHT OF AIR SATD.WATER,G";INPUT W
330 PRINT"RELATIVE HUMIDITY, PERCENT?":INPUT H
340 T1=T+273.18:P2=21.0109-5321.01/T1:P2=EXP(P2)
350 P3=P1-P2*H/100
360 N1=24.3696*LOG(T1)+8576.61/T1-171.854
370 N1= EXP(N1):N1=N1*0.7803*P3/760 :REM VOL N2/CM3 WATER
380 M1=N1*W:REM VOL N2 IN WATER
390 N2=20.5*LOG(T1)+7575.5/T1-138.781
400 N2=EXP(N2):N2=N2*9.56E-3*P3/760000:REM VOL AR/CM3 WATER
410 M2=N2*W:REM VOL AR IN WATER
420 PRINT#1,"TEMP., °C=";T;"ATM. PRESS., MMHG =  ";P1;" CORR.PRESS = ";P3
430 PRINT#1,"REL.HUMIDITY,%=";H;"WT OF WATER,G =   ";W
440 PRINT#1,"SOLUBILITY N2,CM3/G =   ";N1
450 PRINT#1,"SOLUBILITY AR,CM3/G =   ";N2
460 PRINT#1
470 PRINT"CALIBRATE NITROGEN?";INPUTA$
480 IF A$="NO" GOTO 540
490 GOSUB 840
500 V1=M1*((Y(1,2)*R1-X(1,2))/(X(1,1)-Y(1,1)*R1):REM VOL N2 IN TRACER
510 PRINT#1,CHR$(1) "N2 IN TRACER,CM3 = ";V1:PRINT#1
520 PRINT#1,CHR$(1)"28/30 IN TRACER = ";R5
530 PRINT#1,CHR$(1)"36/40 IN TRACER = ";R6
535 PRINT#1:PRINT#1
540 PRINT"CALIBRATE ARGON?";INPUT A$
550 IF A$="NO" GOTO 830
560 GOSUB 1210
570 V2=M2*((Y(2,2)*R2-X(2,2))/(X(2,1)-Y(2,1)*R2):REM VOL AR IN TRACER
580 PRINT#1,CHR$(1)"AR IN TRACER,CM3 = ";V2:PRINT#1
590 IF Q$="YES" GOTO 830
600 PRINT"SAMPLE NAME WITH NGR?":INPUT N$
610 PRINT"COLLECTION DATE ?" : INPUT D2$
620 PRINT"VOL N2 IN TRACER,CM3?";INPUT N1
630 PRINT"VOL AR IN TRACER, CM3 ";INPUT N2
640 PRINT"WEIGHT OF WATER SAMPLE ,G?";INPUT W
650 PRINT"DETERMINE NITROGEN?";INPUT A$
660 IF A$="NO" GOTO 720
670 GOSUB 840
680 V1=N1*((X(1,1)-Y(1,1)*R1)/(Y(1,2)*R1-X(1,2))
690 V1=V1/W
700 PRINT#1,CHR$(1)"N2 CONTENT, CM3/G =   ";V1
710 PRINT#1:PRINT#1,CHR$(1)" N2 IN TRACER,CM3 =   ";N1
720 PRINT"DETERMINE ARGON?";INPUT B$
730 IF B$="NO" GOTO 830
740 GOSUB 1210
750 V2=N2*((X(2,1)-Y(2,1)*R2)/(Y(2,2)*R2-X(2,2))
760 V2=V2/W
770 PRINT#1,CHR$(1)"AR CONTENT,CM3/G =   ";V2
780 PRINT#1;PRINT#1,CHR$(1)" AR IN TRACER,CM3 =   ";N2
790 PRINT#1
800 IF A$ OR B$="NO" GOTO 830
810 R5=V2/V1
820 PRINT#1,CHR$(1)"NITROGEN/ARGON =   ";R5
830 STOP
840 S1=0:N=0
850 PRINT#1,"MLNO.NO.    IC 28E-10  IC 29E-10  IC 30E-10  28/30"
860 OPEN2,4,2
870 PRINT#2,"  99        9999.999    9999.999   9999.999   999.999"
880 FOR I = 1 TO 10
890 PRINT"RATIO MEASUREMENT NUMBER";I
900 PRINT"ENTER 28, 29 AND 30 ION CURRENRTS X1E10":INPUT C1,C2,C3
910 R(I) =(C1+C2/2)/(C3+C2/2):S1=S1+R(I)
920 PRINT#1,I,C1,C2,C3,R(I)
930 NEXT I
```

```
940 PRINT#2:CLOSE2
950 S1 = S1/10
960 FOR I=1TO 10
970 D(I)=R(I)-S1:D(I)=(D(I))12:D1=D1+D(I)
980 NEXT I
990 PRINT#1
1000 PRINT#1,"   ACCEPTABLE VALUES OF 28/30 RATIO"
1010 D1=D1/10:E1=2*SQR(D1)
1020 FORI=1TO10
1030 IF ABS(D(I))>E1 GOTO 1060
1040 N=N+1:R(N)=R(I):S2=S2+R(N)
1050 PRINT#1,"              ";R(N)
1060 NEXTI
1070 S2=S2/N
1080 FOR I=1 TO N
1090 D(I)=R(I)-S2:D(I)=D(I)12:D2=D2+D(I)
1100 NEXTI
1110 D2=D2/N:E2=2*SQR(D2)
1120 PRINT#1
1130 PRINT#1,"FOR ALL 10 VALUES"
1140 PRINT#1,"28/30 AVERAGE=   ";S1;"2 SIGMA=   ";E1
1150 PRINT#1
1160 PRINT#1," FOR ";N;" BEST VALUES "
1170 PRINT#1,"28/30 AVERAGE = ";S2;"2 SIGMA =  ";E2
1180 PRINT#1
1190 R1=S2
1200 RETURN
1210 S1=0:N=0
1220 PRINT#1,"MEAS.NO.    IC  36     IC  40    36/40"
1230 OPEN2,4,2
1240 PRINT#2,"  99         9999.99    9999.99   999.999"
1250 FOR I = 1 TO 10
1260 PRINT"ENTER 36 AND 40 ION CURRENTS";INPUT C1,C2
1270 R(I)=C1/C2:S1=S1+R(I)
1280 PRINT#1,I,C1,C2,R(I)
1290 NEXT I
1300 PRINT#2:CLOSE2
1310 S1 = S1/10
1320 FOR I=1TO 10
1330 D(I)=R(I)-S1:D(I)=D(I)12:D1=D1+D(I)
1340 NEXT I
1350 PRINT#1
1360 PRINT#1,"   ACCEPTABLE VALUES OF 36/40 RATIO"
1370 D1=D1/10:E1=2*SQR(D1)
1380 FORI=1TO10
1390 IF ABS(D(I))>E1 GOTO 1420
1400 N=N+1:R(N)=R(I):S2=S2+R(N)
1410 PRINT#1,"              ";R(N)
1420 NEXTI
1430 S2=S2/N
1440 FOR I=1 TO 10
1450 D(I)=R(I)-S2:D(I)=D(I)12:D2=D2+D(I)
1460 NEXTI
1470 D2=D2/N:E2=2*SQR(D2)
1480 PRINT#1
1490 PRINT#1,"FOR ALL 10 VALUES"
1500 PRINT#1,"36/40 AVERAGE=   ";S1;"2 SIGMA=   ";E1
1510 PRINT#1
1520 PRINT#1,"FOR ";N;" BEST VALUES  "
1530 PRINT#1,"36/40 AVERAGE=";S2;"2 SIGMA=   ";E2
1540 PRINT#1
1550 R2=S2
1560 RETURN
1570 PRINT#1:CLOSE1
1580 END
READY.
```

5. MCCLEOD

```
READY.

 100 V1 = 287.73: REM VOL SYSSTEM AND INLET
 110 V2 = 144.159: REM VOL MACLEOD
 120 V3 = 0.6485: REM VOL BULB BETWEEN CAPS
 130 V4 = 3.1417* 0.024812 :REM VOL/CM SMALL CAP
 140 V5 = 3.1417*0.087512: REM VOL/CM LARGE CAP
 150 L4 = 13.618: REM LENGTH SMALL CAP REF/END
 160 PRINT "ENTER H1(CM)           ":INPUT H1
 170 PRINT "ENTER B1(CM)           ":INPUT B1
 180 PRINT "ENTER L1(CM,L1>B1)     ":INPUT L1
 190 PRINT "ENTER H2(CM)           ":INPUT H2
 200 PRINT "ENTER B2(CM)           ":INPUT B2
 210 PRINT "ENTER L2(CM,L2>B2)     ":INPUT L2
 220 PRINT "ENTER VOLUME OF SAMPLE,CM3":INPUT T
 230 P6 = L1-H1
 240 V6 = (B1-H1)*V5+V3+V4*L4
 250 V6 = V6*P6/76 :REM VOL STP N2+AR
 260 P7 = L2-H2
 270 V7 = (B2-H2)*V4
 280 V7 = V7*P7/76 :REM VOL STP AR
 285 V8 = V6-V7 :REM VOL STP N2
 290 V8 = V8*V1/V2 :REM N2
 310 V7 = V7*V1/V2 :REM AR
 320 R  = V8/V7    :REM N2/AR RATIO
 325 S8 = V8/T:S7=V7/T:REM SOLUBILITIES     .
 330 OPEN1,4:CMD1
 340 PRINT#1,TAB(15);CHR$(1);"N2/AR  MACLEOD "
 350 PRINT#1
 360 PRINT#1,"N2+AR  ,    H1,CM =     "; H1
 370 PRINT#1,"             B1,CM =     ";B1
 380 PRINT#1,"             L1,CM =     "; L1
 390 PRINT#1
 400 PRINT#1,"AR     ,    H2,CM =     "; H2
 410 PRINT#1,"             B2,CM =     "; B2
 420 PRINT#1,"             L2,CM =     "; L2
 430 PRINT#1
 440 PRINT#1,"VOL N2 IN SAMPLE, CM3 =   ";V8
 450 PRINT#1,"VOL AR IN SAMPLE, CM3 =   ";V7
 460 PRINT#1
 470 PRINT#1," N2 IN SOLUTION  =    ";S8;"/CM3"
 480 PRINT#1," AR IN SOLUTION  =    ";S7;"/CM3"
 490 PRINT#1
 500 PRINT#1," N2/AR  =     "; R
 510 PRINT#1:CLOSE1
 520 END
READY.
```

APPENDIX D

Denitrification of dissolved NO_3^- is assumed to occur at two horizons in the recharge profile:

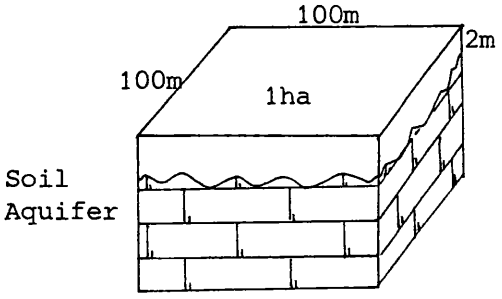
i) within the soil zone;

ii) within the aquifer.

The effect of denitrification of fertilizer on the N_2/Ar ratio of groundwater has been calculated for a model recharge profile.

The Model Recharge Profile

For an area of 1 ha covered to a depth of 2m by soil, the volume of soil air is equivalent to the Storage Pore Space, which for a loam is ≅ 25% of the total volume.



Storage Pore Space
c 25%

$$\text{The volume of soil air} = \frac{\text{Volume of Soil}}{\text{Storage Pore Space}}$$

$$\frac{1 \times 10^4 \times 2 \text{ m}^3}{4} = 5 \times 10^3 \text{ m}^3$$

The volume of nitrogen = p.p. N_2 x volume of soil air

$$0.7803 \times 5 \times 10^3 \text{ m}^3 = 3.9 \times 10^3 \text{ m}^3$$

The volume of argon = p.p. Ar x volume of soil air

$0.00956 \times 5 \times 10^3\ m^3 = 0.0478 \times 10^3\ m^3$

where the N_2/Ar ratio of soil air = 81.58 and the equilibrated groundwater N_2/Ar ratio = 36.8.

i) Within the Soil Zone

If denitrification of fertilizer applied at the rate of 100kg N ha^{-1} occurs within the soil zone, then the N_2/Ar of the groundwater can be calculated as follows:

Conversion of 100kg N ha^{-1} to g NO_3^- ha^{-1}

$$100 \times \frac{62}{14} = 4.4 \times 10^5\ g\ NO_3^-\ ha^{-1}$$

If complete denitrification occurs this will generate

$$\frac{4.4 \times 10^5}{62 \times 2 \times 10^3} = 79.48\ m^3\ N_2\ ha^{-1}$$

The total volume of N_2 in the soil ha^{-1} =

N_2 in soil atmosphere + N_2 from denitrification

$= 3.9 \times 10^3\ m^3 + 79.48 m^3 = 3.98 \times 10^3$ m3

the N_2/Ar ratio of the soil air = 83.24 and the N_2/Ar ratio of groundwater equilibrated at this p.p. = 39.5 (From figure 6.2).

ii) Within the Aquifer

Where denitrification occurs within the aquifer the N_2/Ar of the groundwater can be calculated as follows:

The dissolved N_2 content of air equilibrated groundwater at 10°C

$= 0.014 cm^3/cm^3\ H_2O$

The dissolved Ar content of air equilibrated groundwater at 10°C

$= 3.983 \times 10^{-4}\ cm^3/cm^3\ H_2O$

Conversion of 100kg N ha^{-1} to kg NO_3^- ha^{-1}

$$100 \times \frac{62}{14} = 440Kg\ NO_3^-\ ha^{-1}$$

If the soil is saturated then the volume of water passing from the soil to the aquifer is $5 \times 10^3 m^3$, then the NO_3^- content of recharging groundwater is

$$\frac{440}{5 \times 10^3}\ Kg\ NO_3^-/m^3\ H_2O$$

$$\frac{440 \times 10^3}{5 \times 10^3 \times 10^6} = 88 \times 10^{-6}\ g\ NO_3^-/cm^3\ H_2O$$

$$\frac{88 \times 10^{-6}}{62 \times 2} = 0.7 \times 10^{-6}\ MN_2/cm^3\ H_2O$$

and 1 Gramme Molecular Volume = 22.4 litres

$$\frac{0.7 \times 10^{-6} \times 22.4}{10^{-3}} = 0.0156cm^3N_2.cm^3\ H_2O$$

the total N_2 content per cm^3 water of air equilibrated water + N_2 derived from denitrification

$= 0.014cm^3 + 0.0156cm^3 = 0.0296cm^3N_2/cm^3\ H_2O$

the N_2/Ar ratio = 74.32.

Variation of N_2/Ar Ratio with Soil Depth

Soil Depth	Denitrification	
	Within Soil	Within Aquifer
2m	39.50	74.32
1m	40.25	113.48*
0.5m	42.10	191.82*

* These values are calculated from the volume of recharge equal to the Storage Pore Space and since recharge is continuous these values would probably be much lower. No field observations verify these high ratios.

REFERENCES

1. Wild, A. 1977 Nitrate in drinking water: health hazard unlikely. Nature 268, 197.

2. Anon. 1980 The U.K.'s nitrates "timebomb" - fact or fiction. World Water. Dec. 1980, 21.

3. Wolf, I.A. and Wasserman, A.E. 1972. Nitrates, nitrites and nitrosamines. Science, 177, 15.

4. Young, C.P., Oakes, D.B. and Wilkinson, W.B. Prediction of future nitrate concentrations in groundwater. Groundwater 14, 426.

5. Kreitler, C.W. 1975. Determining the source of nitrate in groundwater by nitrogen isotope studies. Rept. Invest. Bur. Econ. Geol. Univ. Texas, U.S.A. pp83.

6. Odium, E.P. 1971. Fundamentals of Ecology 3rd Ed. N.B. Saunders Co., Philadelphia Pa., U.S.A. pp .

7. Holland, H.P. 1962. Model for the evolution of the earth's atmosphere. in: Petrologic studies. A volume to honour A.F. Buddington. pp447. New York. Geol. Soc. Amer.

8. Bartholomew, W.V. and Clarke, F.E. 1965. Soil Nitrogen, Madison, Wisconsin, U.S.A. Amer. Soc. of Agronomy pp .

9. Nier, A.O. 1950. A redetermination of the relative abundances of the isotopes of carbon, nitrogen, argon and potassium. Phys. Rev. 77, 789.

10. Dole, M., Lane, G.A., Rudd, D.P. and Zaukelies, P.A. 1954. Isotopic composition of atmospheric oxygen and nitrogen. Geochim. Cosmochim. Acta. 6, 65-78.

11. Junk, G. and Svec, H.S. 1958. The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. Geochim. Cosmochim. Acta. 14, 234.

12. Borman, F.H. and Liken, G.E. 1967. Nutrient cycling. Science, 155, 424.

13. Chemical Rubber Co. The Handbook of Chemistry and Physics, 55th Ed. 1974-1975. C.R.C. Press, Cleveland Ohio. Ed. R.C. Weast.

14. Brady, N.C. 1974. The Nature and property of soils 8th Ed. Macmillan Pub. Co. Inc. New York, pp639.

15. Junge, C.E. 1958. The distribution of ammonia and nitrate in rain water over the United States. Trans. Am. Geophys. Union., 39, 241.

16. Eriksson, E. 1952. Composition of atmospheric precipitation 1. Nitrogen compounds. Tellus, 4, 215

17. Angström, A. and Hogberg, L. 1952. On the content of nitrogen (NH_4-N and NO_3-N) in atmospheric pollution. Tellus 4, 31.

18. Junge, C.E. 1963. Air chemistry and radioactivity. Academic Press, New York. pp32.

19. Edmunds, W.M. 1977. Groundwater geochemistry - controls and processes. A Water Research Centre Conference. Groundwater quality, measurement prediction and protection. Reading.

20. Feth, J.H. 1966. Nitrogen compounds in natural water - a review. Water Res. Res. 2, 41

21. Behnke, J. 1975. A summary of the biogeochemistry of nitrogen conpounds in groundwaters. J. of Hydrol. 27, 155.

22. Hem, J.D. 1970. Study and interpretation of the chemical characteristics of natural water. U.S. Geol. Surv. Water Supply Paper. 1473. Washington D.C., U.S.A. 2nd Ed. pp363.

23. Rankama, K. and Sahama, Th.G. 1968. Geochemistry. The University of Chicago Press, Chicago, U.S.A. 6th Imp. pp912.

24. Silver, B.A. and Fielden, J.R. 1980. Distribution and probable source of nitrate in groundwater of Paradise Valley, Arizona. Groundwater 18, 244.

25. Kharaka, Y.K. and Berry, F.A.F. 1973. Simultaneous flow of water and solutes through geological membranes. 1. Experimental investigation. Geochim. Cosmochim. Acta. 31, 2577.

26. Bieri, R.H. 1974. Dissolved conservative gases in seawater. in: The Sea, 5, Ed. D. Goldberg, Wiley and Sons, New York. pp895.

27. Lanning, A. 1930. The solubilities of He, Ne and Ar in water and some organic solvents. J. Phys. Chem. 42, 68.

28. Rakestraw, N.W. and Emmel, V.M. 1938. The solubility of nitrogen and argon in sea water. J. Phys. Chem. 42, 1211

29. Morrison, T.J. and Johnstone, N.B. 1954. Solubilities of inert gases in water. J. Chem. Soc., 3441.

30. Himmelblau, D.M. 1960. Solubilities of inert gases in water. J. Chem. Engng. Data. 5, 10.

31. Benson, B.B. and Parker, P.D.M. 1961. Relation among the solubilities of N_2, Ar and O_2 in distilled water and sea water. J. Phys. Chem. 65, 1489.

32. Hamberg, A. 1886. Beitrage zur Chemie des Meerwasser. J. Prakt Chem. 33, 433.

33. Fox, C.J.J. 1909. On the coefficients of absorption of nitrogen and oxygen in distilled water and sea water, and of atmospheric carbonic acid in sea water. Trans. Faraday Soc. 5, 68.

34. Adeney, W.E. and Becker, H.G. 1919. The determination of the rate of absorption of nitrogen and oxygen by water. Proc. R. Dublin Soc. 15, 609.

35. Winkler, L.W. 1906. Gesetzmassigkeit bei der Absorption der Gase in Flussigkeiten. Z. Physik. Chem. 55, 344.

36. Morrison, T.J. and Billet, F. 1952. The salting-out of non-electrolytes. Part II. The effect of variation in non-electrolyte. J. Chem. Soc. 3819.

37. Klots, C.E. and Benson, B.B. 1963. Solubilities of nitrogen, oxygen and argon in distilled water. J. Marine Res. 21, 48.

38. Douglas, E. 1964. Solubilities of oxygen, argon and nitrogen in distilled water. J. Phys. Cehm. 68, 169.

39. Murray, C.N., Riley, J.P. and Wilson, T.R.S. 1969. The solubility of gases in distilled water and sea water -1. Nitrogen. Deep Sea Res. 16, 297.

40. Weiss, R.F. 1970. The solubility of N_2, O_2, Ar in water and sea water. Deep Sea Res. 17, 721.

41. Benson, B.B. and Krause, D. 1976. Empirical laws for dilute aqueous solution of non-polar gases. J. Chem. Phys. 64, 639.

42. Konig, H. 1963. Uber die Ioslichkeit der Edelgase in Meerwasser. Z. Naturforsch, 18A, 363.

43. Douglas, E. 1965. Solubilities of argon and nitrogen in sea water. J. Phys. Chem. 69, 2608.

44. Morris, J.C. and Stumm, W. 1976. Redox equilibria and measurements of potentials in the aquatic environment. in: Equilibrium concepts in natural water systems. Amer. Chem. Soc. Advances in Chemistry Ser., 67, 270.

45. Delwiche, C.C. 1970. The nitrogen cycle. Sci. Amer. 223, 137.

46. Champ, D.R. and Gulens, J. 1979. Oxidation-reduction sequences in groundwater flow systems. Can. J. Earth Sci. 16, 12.

47. Edmunds, W.M. 1973. Trace element variation across an oxidation-reduction barrier in a limestone aquifer. Proc. Symp. Hydrogeochem. Biogeochem. Tokyo 1970. Ed. Ingerson, E. Clarke Co., Washington, Vol 1, 500.

48. Ineson, J. and Dawning, R.A. 1963. Changes in the chemistry of groundwaters of the Chalk passing beneath argillaceous strata. Bull Geol. Gt. Brit. 20, 176.

49. Dawning, R.A. and Williams, B.P.J. 1969. The groundwater hydrology of the Lincolnshire Limestone. Water Resources Board. Reading. pp160.

50. Craig, H. 1968. Isotope separation by carrier diffusion. Science. 159, 93.

51. Stahl, W., Wollanke, G. and Boigk, H. 1975. Carbon and nitrogen isotope data of upper carboniferous and Rotliegende natural gases from North Germany and their relationship to the maturity of the organic source material. 7th Int. Meet. Org. Chem. Madrid, September 1975.

52. Benson, B.B. and Parker, P.D.M. 1961. N_2/Ar and N isotope ratios in aerobic sea water. Deep Sea Res. 7, 237.

53. Klots, C.E. and Benson, B.B. 1963. Isotope effect in the solution of oxygen and nitrogen in distilled water. J. Chem. Phys. 38, 890.

54. Fryer, H.D. and Aly, A.I.M. 1975. Nitrogen - 15 studies on identifying fertilizer excess in environmental systems. In isotope ratios as pollutant source and behaviour indicators. Proc. Symp. I.A.E.A. and F.A.O. Vienna 1974. I.A.E.A., 489, pp .

55. London, M. 1961. Separation of Isotopes. Newnes, London. pp489.

56. Delwiche, C.C. and Steyn, P.L. 1970. Nitrogen isotope fractionation in soils and microbial reactions. Env. Sci. Tech. 4, 929.

57. Urey, M.C. and Greiff, L.J. 1935. Isotopic exchange equilbria. Am. Chem. Soc. Jour. 57, 321.

58. Cook, F.D. and Wellman, R.P. 1973. Nitrogen isotope fractionation in the nitrogen cycle. I.A.G.C. Symposium. Biogeochem. Ed. Ingerson E. Vol 2, 49.

59. Hoering, T.C. 1958. Cosmological and geological implications of isotope ratio variations, Sect. V: Isotopic abundances of lighter elements. Nucl. Sci. Ser. Rep. 23. Nat. Acad. Sci.; Nat. Res. Council Publ. 572, 161

60. Hoering, T.C. and Ford, H.T. 1960. Isotope effect in the fixation of nitrogen by Azobacter. J. Amer. Chem. Soc. 82, 376.

61. Laishley, E.J., McCready, R.G.L., Bryant, R., Krouse, H.R. 1975. Stable isotope fractionation by Clostrifium pasteur ianum. 2nd Int. Symp. Biogeochemistry. Hamilton. Ont. Canada. 1975.

62. Amarger, N., Mariotti, A. and Mariotti, F. 1977. Essai d'estimation du taux d'azote dixé symbiotiquement chez le lupin par le traçage isotopique naturel (^{15}N) C.R. Acad. Sci. Paris. Ser. D.284:2179.

63. Riga, A., Van Praag, H.J. and Brigade, N. 1971. Rapport isotopique naturel de l'azote dans quelque sols forestiers et agricles de Belgique soumis a divers traitments culturaux. Geoderma 6, 213.

64. Feigin, A.D., Kohl, D.H., Shearer, G.B. and Commoner, B. 1974. Variation in the natural nitrogen - 15 abundance in nitrate mineralized during incubation of several Illinois soils. Soil. Sci. Soc. Amer. Proc. 38, 90.

65. Freyer, H.D. and Aly, A.I.M. 1974. Nitrogen - 15 variations in fertilizer nitrogen. J. Env. Qual. 3, 405.

66. Focht, D.D. 1973. Isotope fractionation of ^{15}N and ^{14}N in microbiological nitrogen transformations: a theoretical model. J. Env. Qual. 2, 247.

67. Mariotti, A. and Létolle, R. 1977. Application de l'étude isotopique de l'azote an hydrologie et en hydrogeology - analyse des résultats abtenus sur un example précis: le Bassin de Mélarchez (Seine et Marne, France). J. Hydrol. 33, 157.

68. Myaka, Y. and Wada, K. 1971. The isotope effect on the nitrogen in biochemical oxidation-reduction reactions. Rec. Oceanogr. Works Japan 11, 1.

69. Shearer, G., Duffy, J., Kohl, D.H. and Commoner, B. 1974. A steady state model of isotopic fractionation accompanying nitrogen transformations in soils. Soil Sci. Soc. Amer. Proc. 38, 315.

70. Wellman, R.P., Cooke, F.D. and Krause, H.R. 1968. Nitrogen 15: microbiological alteration of abundance Science. 161., 269.

71. Urey, H.C. 1947. Thermodynamic properties of isotopic substances. J. Chem. Soc., 562.

72. Wada, E., Kadonaga, T. and Matsuo, S. 1975. ^{15}N abundance in naturally occurring substances and global assessment of denitrifications from isotopic viewpoint. Geochem. Journal of Japan. 9, 139.

73. Cline, J.D. and Kaplan, I.R. 1975. Isotopic fractionation of dissolved nitrate during dentrification in the eastern tropical North Pacific Ocean. Marine Chemistry. 3, 271.

74. Blackmer, A.M. and Bremner, J.M. 1977. Nitrogen isotope discrimination in denitrification of NO_3 in soils. Soil Biol. Biochem. 9, 73.

75. Richet, P., Bottinga, Y. and Javoy, M. 1977. A review of hydrogen, carbon, nitrogen, oxygen, sulphur and chlorine stable isotope fractionation among gaseous molecules. Annu. Rev. Earth. Planet. Sci. 5, 65.

76. Hoering, T.C. 1956. Variation in the nitrogen abundance. Proc. 2nd Conf. Nuclear Processes in Geologic Settings. 39.

77. McQueen, J.H. 1950. Isotopic separation due to settling in the atmosphere. Phys. Rev. 80, 100.

78. Scalan, R.S. 1959. The isotopic composition, concentration and chemical state of nitrogen in igneous rocks. Ph.D. Thesis, Univ. Arkansas, U.S.S. University Microfilms. Ann. Arbor. Michigan. Microfilm. 59-1379.

79. Mayne, K.I. 1957. Natural variations in the nitrogen abundance ratio in igneous rocks. Geochem. Cosmochim. Acta. 12, 185

80. Lord Rayleigh. 1939. Nitrogen argon and neon in the earth's crust with applications to cosmology. Proc. Roy. Soc. London (A). 170, 451.

81. Parwell, A., Ryhage, R. and Wickman, F. 1957. Natural variation in the relative abundances of nitrogen isotopes. Geochim. Cosmochim. Acta. 11, 165.

82. Hoering, T. 1955. Variations in nitrogen - 15 abundance in naturally occurring substances. Science 122, 1233.

83. Bokhoven, C. and Theuwen, H.J. 1966. Determination of the abundance of carbon and nitrogen isotopes in Dutch coals and natural gas. Nature 211, 927.

84. Hoering, T. and Moore, H.E. 1957. The isotopic composition of the nitrogen in natural gases and associated crude oils. Geochim. Cosmochim. Acta. 13, 225.

85. Heoring, T. 1957. The isotopic composition of the ammonia and the nitrate ion in rain. Geochim. Cosmochim. Acta. 12, 97.

86. Myaka, Y. and Wada, E. 1967. The abundance ratio of $^{15}N/^{14}N$ in marine environments. Recs. of Oceanog. Works in Japan. 9, 37.

87. Batard, F., Bambron, J.C., Bosch, B., Marche, A. and Risler, J.J. 1982. Isotopic identification of gases of a deep origin in French thermomineral waters. J. Hydrol. 56, 1.

88. Sweeney, R.E. and Kaplan, I.R. 1980. Natural abundances of ^{15}N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. Marine Chemistry 9, 81.

89. Hauck, R.D. 1973. Nitrogen tracers in nitrogen cycle studies - past use and future needs. J. Env. Qual. 2, 317.

90. Edwards, A.P. 1973. Isotopic tracer techniques for identification of sources of NO_3 pollution. J. Env. Qual. 2, 382.

91. Black, A.S. and Waring, S.A. 1977. The natural abundance of ^{15}N in the soil water system of a small catchment area. Aust. J. Soil Res. 15, 51.

92. Chang, H.H., Bremner, J.M. and Edwards, A.P. 1964. Variations of nitrogen - 15 abundance in soils. Science 146, 1574.

93. Riga, A., Von Praag, H.J. and Brigade, N. 1971. Rapport isotopique naturel de l'azote dans quelques sols forestiers et agricoles de Belgique soumis a divers traitements culturaux. Geoderma 6, 213.

94. Bremner, J.M. and Tabatabai, M.A. 1973. Nitrogen - 15 enrichment of soils and soil derived nitrate. J. Env. Qual. 2, 363.

95. Rennie, D.A., Paul, E.A. and Johns, L.E. 1976. Natural nitrogen - 15 abundances of soil and plant samples. Can. J. Soil Sci. 56, 43.

96. Rennie, D.A. and Paul, E.A. Nitrogen isotope ratios in surface and sub-surface soil horizons.

97. Shearer, G.B., Daniel, H., Kohl, D.H. and Sen Hsiung Chlen. 1978. The nitrogen - 15 abundance in a wide variety of soils. Soil Sci. Soc. Am. J. 42, 899.

98. Kohl, D.H., Shearer, G.B. and Commoner, B. 1971. Fertilizer nitrogen: contribution of NO_3 in surface water in a cornbelt watershed. Science 174, 1331.

99. Karamanos, R.E. and Rennie, D.A. 1980. Variations in natural nitrogen - 15 abundance as an aid in tracing fertilizer nitrogen transformations. Soil Sci. Soc. Am. J. 44, 57.

100. Karamanos, R.E., Voroney, R.P. and Rennie, D.A. 1981. Variations in natural N-15 abundance of central Saskatchewan soils. Soil Sci. Soc. Am. J. 45, 826.

101. Freyer, H.D. and Aly, A.I.M. 1975. Nitrogen - 15 studies in identifying fertilizer excess in environmental systems in: Isotope ratios as pollutant sources and behaviour indicators. Proc. Symp. Vienna. Nov. 1974. Joint I.A.E.A. and F.A.O. pp21-33.

102. Bremner, J.M., Cheng, H.M. and Edwards, A.P. 1966. Assumptions and errors in nitrogen - 15 tracer research in: The use of isotope in soild organic matter studies. (Report of F.A.O. - I.A.E.A. Technical meeting, Brunswick, Volkenrode, 1962). Pergamon Press, New York. pp429-445.

103. Feigin, A.D., Shearer, G.B., Kohl, D.H. and Commoner, B. 1974. The amount and nitrogen - 15 content of nitrate in soild profiles from two central Illinois fields in a corn-soy bean rotation. Soil Sci. Sco. Amer. Proc. 38, 465.

104. Hauck, R.D. et al 1972. Use of variation in nitrogen isotope abundance for environmental studies: a questionable approach. Science 177, 453.

105. Meints, V.W., Boone, L.V. and Kurtz, L.T. 1975. Natural ^{15}N abundance in soil, leaves and grain as influences by long term additions of fertilizer N at several rates. J. Env. Qual. 4, 486.

106. Chichester, F.W. and Smith, S.J. 1978. Disposition of ^{15}N labelled fertilizer. Nitrate applied during corn culture in field lysimeters. J. Env. Qual. 7, 227.

107. Hauck, R.D., Melsted, S.W. and Yankwich, P.E. 1958. Use of N-isotope distribution in nitrogen gas in the study of denitrifcation. Soil Sci. 86, 287.

108. Cady, F.B. and Bartholomew, M.V. 1960. Sequential products of anaerobic denitrification in Norfolk soil material. Soil Sci. Soc. Amer. Proc. 24, 477.

109. Owen, L.D. 1960. Nitrogen movement and transformation in soils evaluated by a lysimeter study utilizing isotopic nitrogen. Soil Sci. Soc. Amer. Proc. 24, 372.

110. Dowdell, R.J., Burford, J.R. and Crees, R. 1979. Losses of nitrous oxide dissolved in drainage water from agricultural land. Nature. 278, 342.

111. Lipschultz, F., Zafirion, O.C., Wofsy, S.C., McElroy, H.B., Valois, F.W. and Watson, S.W. 1981. Production of NO and N_2O by soil nitrifying bacteria. Nature 294, 641.

112. Oren, A. and Blackburen, T.H. 1979. Estimation of sediment denitrification rates at in situ nitrate concentrations. Applied Env. Microbiol. 37, 174.

113. Young, C.P. and Hall, E.S. 1976. Investigation into factors affecting the nitrate content of groundwater. Proc. Water Research Centre Conf. on Groundwater Quality - Measurement, Prediction and Protection , Reading.

114. Cooke, G.W. and Williams, R.J.B. 1970. Losses of nitrogen and phosphorous from agricultural land. Water Treat. and Exam. 19, 253.

115. Kreitler, C.W. and Jones, D.C. 1975. Natural soil nitrate the cause of the NO_3 contamination in Runnels County, Texas. Groundwater 13, 53.

116. Reinhorn, T. and Avnimlech, Y. 1974. Nitrogen release associated with the decrease in soil organic matter in newly cultivated soils. J. Env. Qual. 3, 118.

117. Olsen, R.J., Hensler, R.F., Attoe Witzer and Peterson, L.A. 1970. Fertilizer nitrogen and crop rotation in relation to movement of NO_3N through soil profiles. Soil Sci. Soc. Amer. Proc. 34, 448.

118. Kolenbrander, G.R. 1975. Nitrogen in organic matter and fertilizer as a source of pollution. In Proc. Int. Ass. Water Poll. Res. Specialised Conf. Nitrogen as a Water Pollutant. Copenhagen.

119. Davey, K.W. 1970. An investigation into the nitrate pollution of Chalk borehole water supplies. N Lindsey Water Board, Scunthorpe.

120. Greene, L.A. and Walker, P. 1970. Nitrate pollution of Chalk Waters. Water Treat. and Exam. 19, 169.

121. Satchell, R.L.H. and Edworthy, K.J. 1972. Artificial recharge: Bunter sandstone, Trent Research Programme. V 7. Water Resources Board, Reading.

122. Foster, S.S.D. and Crease, R.I. 1974. Nitrate pollution of chalk groundwater in East Yorkshire - a hydrogeological appraisal. J. Inst. Water Eng. 28, 178.

123. Foster, S.S.D. 1976. The vulnerability of British groundwater resources to pollution by agricultural leachates in: Tech. Bull. Ministry Agric., Fish and Food, London. No. 32.

124. Rible, J.M., Nash, P.A., Pratt, P.F. and Lund, L.J. 1976. Sampling the unsaturated zone of irrigated lands for reliable estimates of nitrate concentration. Soil Sci. Soc. Amer. Proc. 40, 566.

125. Wellings, S.R. and Bell, J.P. 1980. Measurement of water and nitrate in the unsaturated zone of Upper Chalk near Winchester, Hants., England. J. Hydrol. 48, 119.

126. Wellings, S.R. and Bell, J.P. 1982. Physical controls of water movement in the unsaturated zone. Q.J. Eng. Geol. Land. 15, 235.

128. Kreitler, C.W. 1974. Determining the source of nitrate in groundwater by nitrogen isotope studies. Thesis Univ. of Texas, Austin, Texas, U.S.A.

129. Kreitler, C.W., Ragone, S.E. and Katz, B.G. 1978. $^{15}N/^{14}N$ Ratios of groundwater nitrate, Long Island, New York. Groundwater 16, 404.

130. Kreitler, C.W. 1979. Nitrogen isotope ratio studies of soil and groundwater nitrate from alluvial fan aquifers in Texas. J. Hydrol. 42, 147.

131. Gormley, J.R. and Spalding, R.F. 1979. Sources and concentrations of nitrate nitrogen in groundwater in the Central Platte Region, Nebraska, Groundwater 17, 291.

132. Letolle, R. and Marriotti, A. 1974. Utilization des variation naturelle d'abundance de l'azote - 15 comme traceur en hydrogeologue. I.A.E.A. SM. 182/40. Isotopes in Hydrology.

134. Kimmell, G.E. 1972. Nitrogen content of groundwater in Kings County, Long Island, New York. U.S.Geol. Survey. Prof. Paper. 800-D. pD199.

135. Andrews, J.N. and Lee, D.J. 1979. Inert gases in groundwater from the Bunker Sandstone of England as indiactors of age and palae odimatic trends. J. Hydrol. 41, 233.

136. Herzberg, O. and Mazor, E. 1979. Hydrological applications of noble gases and temperature measurements in underground water systems: Examples from Israel J. Hydrol. 41, 217.

137. Weiss, R F. and Craig, H. 1971. Precise shipboard determination of dissolved nitrogen, oxygen, argon and total inorganic carbon by gas chromatography. Deep Sea Res. 20, 291.

138. Heaton, T.H.E. and Vogel, J.C. 1980. "Excess Air" in groundwater. J. Hydrol. 50, 201.

139. Wilson, L.G. and Luthin, J.N. 1963. Effects of air flow ahead of the wetting front on infiltration. Soil Sci. 96, 137.

140. Topp, G.C. 1971. Soil water hysteresis: the domain theory extended to pore interaction conditions. Soil Sci. Soc. Amer. Proc. 35, 219.

141. Dixon, R.M. and Lindens, D.R. 1972. Soil air pressure and water infiltration under border irrigation. Soil Sci. Soc. Amer. Proc. 36, 948.

142. Vachaud, G., Gauder, J.P. and Kiraz, V. 1974. Air and water flow during ponded infiltration in a vertical bounded column of soil. J. Hydrol. 22, 89.

143. Enns, T., Scholander, P.F. and Bradstreet, E.D. 1965. Effects of hydrostatic pressure on gases dissolved in water. J Phys. Chem, 69, 389.

145. Vogel, J.C., Talma, A.A., Heaton, T.H.E. 1980. Gaseous nitrogen as evidence for denitrification in groundwater. J. Hydrol. 50, 191.

146. Rightmire, C.T. 1978. Changes in formation gas composition and isotopic content as indicators of unsaturated zone chemical reactions related to recharge events. Proc. Symp. Neuhenberg, June 1978. Isotopic Hydrology I.A.E.A., Vienna, Vol 2, 711.

147. Richards, F.A. and Benson, B.B. 1961. N/Ar and N_2 ratios in two aerobic environments. Deep Sea Res. 7, 254-264.

148. Edmunds, W.M. 1975. Water quality sampling and field chemical measurements for overseas hydrogeological surveys. Rep. No. W.D./ST/75/14. I.G.S. Hydrogeological Dept. 13pp.

149. Zobell, C.E. 1946. Studies of redox potentials of marine sediments. Am. Assoc. Petroleum Geologists Bull. 30, 477.

150. Orion. 1978. Instruction manual; platinum redox electrode, model 96-78. Orion Research Incorporated, Cambridge, Mass. U.S.A. pp12.

151. Wood, W.W. 1976. Technique of water resources investigation of the U.S. Geological Survey. "Guidelines for collection and field analysis of groundwater samples for selected unstable constituents. U.S. Dept. of Interior. BKI. Chap. D2.

152. American Public Health Association. 1971. Standard methods for examination of water and waste water. Am. Pub. Health Assoc. Washington D.C., 874pp.

153. E.I.L. (Electronic Instruments Limited). 1972. Operation Manual. Dissolved Oxygen Electrode Models A15A, 1521, A94T, Chertsey, Surrey.

154. Miles, D.L. 1977. Influence of Collection and Storage Procedures on the Nitrate and Phosphate Content of Groundwater Samples. Rep. No. WD/ST/77/10. I.G.S. Hydrogeological Dept. Wallingford, Oxon.

155. Sullivan, W.T. 1975. Experience with nitrogen compounds in natural waters. J. Am. Water Works Assoc. 67, 146.

157. Rainwater, F.H., Thatcher, L.L. 1960. Methods for Collection and Analysis of Water Samples. U.S. Geol. Survey. Water Supply Paper 1454. pp301.

158. Lee, D.J. 1980. Radium, Radan and Inert Gases in Groundwaters and Rocks as Geochemical Tracers. Ph.D. Thesis. University of Bath.

159. Williams, W.J. 1979 Handbook of Anion Determination. Butterworths, London. pp630.

160. Bremner, J.M. 1965. Steam distillatin methods for determination of ammonium nitrate and nitrite. Anal. Chim. Acta. 32, 485.

161. Barnes, H. 1950. A modified 2, 4-xylenol method for nitrate estimation. Analyst. 75, 388.

162. Andrews, D.W.W. 1964. Sensitive method for determining nitrate in water with 2, 6-xylenol. Analyst. 89, 730.

163. Montgomery, H.A.C. and Dymock, J.F. 1962. The Rapid Determination of Nitrate in Fresh and Saline Waters. Analyst. 87, 374.

164. Jenkins, D. and Medsker, L.L. 1964. Brucine method for the determination of nitrate in ocean, estuarine and fresh waters. Anal. Chem. 36, 610.

165. Mullin, J.B. and Riley, J.P. 1955. The spectrophotometric determination of nitrate in natural waters, with particular reference to sea water. Anal. Chim, Acta. 12, 464.

166. Chow, F.J. and Johnson, M.S. 1962. Determination of nitrate in sea water. Anal. Chim. Acta. 27, 441.

167. Nydahl, F. 1976. On the optimum conditions for the reduction of nitrate to nitrite by cadmium. Talanta, 23, 349.

168. Strickland, J.D.H. and Parsons, T.R. 1968. A manual of sea water analysis, 2nd Ed. Fish. Res. Board Can. Ottowa Bull No. 168.

169. Armstrong, F.A.J. 1963. Determination of nitrate in water by ultraviolet spectrometry. Anal Chem. 35, 1292.

170. Miles, D.L. and Espejo, C. 1970. Comparison between ultraviolet spectrophotometric procedure and the 2, 4-xylenol method for the determination of nitrate in groundwaters of low salinity. Analyst. 102, 104.

171. Davison, W. and Woof, C. 1979. Interface studies in the batch determination of nitrate in freshwater by reduction with Cadmium in nitrate. Analyst. 104, 385.

172. Davison, W. and Woof, C. 1978. Comparison of Different Froms of Cadmium as Reducing Agents for the Batch Determination of Nitrate. Analyst. 103, 403.

173. Greiss, P. 1879. Bernerkungen zu der Abhandlung der HH Weselsky und Benedikt Uebereinige Azoverbindungen Ber. 12, 427.

174. Ilsovay, M.L. 1889. Bull. Soc. Chim. 2, 317.

175. Truesdale, V.W. 1971. A modified spectrophotometric method for the determination of ammonia (and amino acids) in natural waters, with particular reference to sea water. Analyst. 96, 584.

176. Matsunaga, K. and Nishimura, M. 1974. A rapid and sensitive method for determination of submicrogran amounts of ammonia in fresh and sea waters. Anal. Chim. Acta. 73, 204.

177. Roskam, R. Th. and De Laugen, D. 1964. A simple colorimetric method for the determination of ammonia in sea water. Anal. Chim. Acta. 30, 56.

178. Solovzano, L. 1969. Determination of ammonia in natural waters by Phenothypochlorite Method. Limnol. Oceanogr. 14, 799.

179. Gillbricht, M. 1961. Detection of ammonia in sea water. Helgoland, wiss Meeresunters. 8, 58.

180. Matsudria, C and Tsuda, T. 1957. Studies on the analytical method of ammonia and organic nitrogen in sea water. Tohuku J. Agr. Res. 8, 37.

181. Richards, F.A. and Kletsch, R.A. 1964. Recent researches in the fields of hydrosphere, atmosphere nuclear geochemistry. Sugawara Festival Volumes, Marrizen, Tokyo.

182. Pitwell, P. 1975. The determination of hydroxylamine in Ethiopia Rivers and Lakes. Mickrochimica Acta. (Wien). 11, 425.

183. Tanaka, M. 1953. Occurrence of Hydroxylamine in Lake Waters as an intermediate in Bacterial Reduction of NO_3. Nature. 171, 1161.

184. Stanier, R.Y., Palleroni, J.J. and Doudoroft, M. 1966. The Aerobic pseudomonads: a taxonomic study. J. Gen. Micro Biol. 43, 159.

185. Barjac, De. H. 1952. La puissance denitrificate du sol. Mise au point d'une technique d'evaluation. Annls. List. Pasteur, Paris. 83, 207.

186. King, E.O., Ward, H.K. and Ramey, D.E. 1954. Two simple media for the demonstration of pyocyanin and fluorescin. J. Lab. Clin. Med. 44, 301.

187. Hugh, R. and Leifons, E. 1953. The taxonomic significance of fermentative versus oxidative metabolism of carbohydrates by various Gram negative Bacteria. J. Bact. 66, 24.

188. Kovacs, N. 1956. Identification of Pseudomonas pycocyanea by oxidase reaction. Nature 178, 703.

189. Miller, K. and Neville, M.E. 1976. Evaluation of alternate coupling reagents to replace a naphthylamine for the Microbios. 17, 207.

190. Hamm, R.E. and Thompson, T.G. 1941. Dissolved N in the sea water of the northeast Pacific - total CO_2 and dissolved O. J. Mar. Res. 4, 11.

191. Rakestraw, N.W. and Emmel, V.H. 1938. The solubilities of N and Ar in sea water. J. Phys. Chem. 42, 1211.

192. Craig, H., Weiss, R.F. and Clarke, W.B. 1967. Dissolved gases in the equations and south Pacific ocean. J. Geophys. Res. 72, 6165.

193. Atkinson, L.P. 1972. Electrolytic Calibration Technique for Dissolved Nitrogen Determination in sea water by on-stream stripping Gas Chromatography. Anal. Chem. 44, 885.

194. Linnenbom, V.J., Swinnerton, J.W. and Cheek, C.H. 1965. Evaluation of gas chromatography for the determination of dissolved gases in sea water. Oceaog. Sci. Eng. Trans. Joint Conf. Marine Tech. Soc. Am. Soc. Oceanog. 1009-1032.

195. Fielder, R. and Proksch, G. 1975. The determination of Nitrogen - 15 by emission and mass spectrometry in Biochemical analysis: A review. Anal. Chim. Act. 78, 1.

195a. Martens, C. 1974. A method for measuring dissolved gases in pore waters. Lusinol. Oceanog. 19, 525.

196. Cline, J.D. and Ben-Yaakov, S. 1973. N_2/Ar ratios by difference thermal conductivity. Deep Sea Res. 20, 763.

196a. Freidel, R.A., Sharkey, Jr. A.G., Schultz, J.L. and Humbert, C.R. 1953. Mais spectrometric analyses of mixtures containing nitrogen dioxide. Anal. Chem. 25, 1314.

197. Swinnerton, J.W., Linnenbom, V.J. and Cheek, C.H. 1962. Raised sampling procedure for determination of dissolved gases in solution by gas chromatography. Anal. Chem. 34, 1509.

198. Darling, W.G. 1981. The Analysis of Free and Dissolved Gases by Chromoatography. Reps No. WD/ST/81/7 I.G.S. Hydrology Unit.

199. Walker, J.A.J., France, E.D. 1969. The determination of dissolved gases in water by continuous stripping and gas chromatography.

200. Williams, D.D. and Miller R.R. 1962. Instrument for on-stream stripping and gas chromatographic determination of dissolved gases in liquid. Anal. Chem. 34, 657.

201. Thompson, B. 1977. Fundamentals of gas analyst by gas chromatography. Varian. pp132. Lib. Cong. Cat. No. 77-71187. U.S.A.

202. Karlsson, B.M. 1966. Heat treatment of molecular sieves for direct separation of Ar and O_2 at Room Temperature by gas chromatography. Anal. Chem. 38, 668.

203. Thouzeau, F. 1976. Separation du Krypton de l'azote par chromatographie en phase gaseuse à temperature ambiante. Utilization par l'analyse des gas produits par fission. Chromatographia 9, 506.

204. Walker, A. 1966. Chromatographic separation of Argon and Oxygen using molecular sieves. Nature. 209, 197.

205. Heaton, T.H.E. 1980. Personal communication.

206. Bath, A. 1981. Unpublished.

207. Martin, A.E., and Ross, P.J. 1968. Significance of Errors in ^{15}N Measurements in Soil: Plant Research. Proc. Int. Congr. Soil Sci. Trans. 9th Adelaide, Aus. 521-529.

208. Bath, A. 1981. Personal communication.

209. Bremner, J.M. 1965. Isotope analysis of N in ^{15}N tracer investigations in methods of soil analysis pt. 2. Chemical and Microbiological properties. Madison, Wisc. Soc. Agronomy. pp1256-1285.

210. Capindale, J. and Tomlin, D. 1957. Mass spectrometric analysis of elemental nitrogen. Nature. 180, 701.

211. Sims, A.P. and Cockin, E.C. 1958. Assay of isotopic nitrogen by mass spectrometer. Nature. 181, 474.

212. Ross, P.J., Martin, A.E. 1970. Rapid procedure for preparing gas sample for nitrogen - 15 determination. Analyst. 95, 817.

213. Husser, R., Habfast, K. and Von Bradke, M. 1960. Z. Analyst. Chem. 176, 429.

214. Kent, P.E. 1966. A review of the correlation of the Lincolnshire Limestone (Inferior) Trans. Leicester Lit. Phil. Soc. 60, 57.

215. Rushton, K R. 1975. Aquifer analysis of the Lincolnshire Limestone using mathematical models. J. Inst. Wat. Eng. Sci. 29, 373.

216. Fox, I.A. and Rushton, K.R. 1976. Rapid recharge in a limestone aquifer. Groundwater. 14, 21.

217. Burgess, D.B. and Smith, E.J. 1979. The effects of groundwater development. The case of the South Lincolnshire Limestone Chap. 5 in Mans impact on the hydrological cycle in the UK. Ed. 9 E. Hollis. Geoabstracts, Norwich. UK. 278pp.

218. Day, J.B.W. et al. 1967. Hydrological map of North and East Lincolnshire. I.G.S. Publication. London.

219. Walton, N.R.G. 1980. Summary of unpublished hydrogeochemical data on the Linolnshire Limestone for studies between 1969 and 1980. I.G.S. Unpub. Rep. WD/ST/80/9.

220. Lamont, P. 1959. A soft water zone in the Lincolnshire Limestone. J. Brit. Water Assoc. 41, 48.

221. Edmunds, W.M. and Walton, N.R.G. 1982. The Lincolnshire Limestone Hydrogeochemical Evolution over a ten-year period. To be published.

222. Smith, E.J. 1979. (Personal communication with Anglian Water Authority Data).

223. Cook, J.M. and Miles, D.L. Methods for the analysis of groundwaters. I.G.S. Rep. Series Rep. No 80/5.

224. Foster, S.S.D. and Young, C.P. 1981. Effects of Agricultural Land Use on Groundwater Quality with Special Reference to Nitrate in A Survey of British Hydrogeology. The Royal Society, p47. pp290.

225. Lawrence, A.R., Lloyd, J.W. and Marsh, J.M. 1976. Hydrochemistry and groundwater mixing in part of the Linconshire Limestone Aquifer, England. Groundwater. 14, 320.

226. Downing, R.A., D.B. Smith, F.J. Pearson, R.A. Monkhase and R.L. Otler. 1977. The age of groundwater in the Lincolnshire Limestone, England and its relevance to the flow mechanism. J. Hydrol. 33, 201.

227. Anglian Water Authority Hydrogeochemical Records 1976-1978.

228. Water Resources Board. 1972. The hydrogeology of the London Basin. W.R.B. Reading. 139pp.

229. Morel, E.H. 1980. The use of a numerical model in the management of the Chalk aquifer in the Upper Thames Basin. Q.J. Eng. Geol. Lond. 13, 153.

230. Black, M. 1953. The constitution of the Chalk, Proc. Geol. Soc. Lond. 1499, 181.

231. Hancock, J.M. and Kennedy, W.J. 1967. Photographs of hard and soft Chalks taken with a scanning electron microscope. Proc. Geol. Soc. Land. 1643, 249.

232. Morgan-Jones, M. 1977. Mineralogy of the Non-Carbonate Material from the Chalk of Berkshire and Oxfordshire, England. Clay Minerals. 12, 331.

233. Edmunds, W.M., Lovelock, P.E.R. and Gray, D.A. 1973. Interstitial Water Chemistry and Aquifer properties in the Upper and Middle Chalk of Berkshire, England.

234. Foster, S.S.D. and Milton, V.A. 1974. The permeability and storage of an unconfined Chalk aquifer 1974. Hydrol. Sci. Bulletin. 19, 485.

235. Smith, D.B., Wearn, P.L., Richards, H.J. and Rowe, P.C. 1970. Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium isotope. Hydrology p73. Int. Atomic Energy Agency. Vienna.

236. Downing, R.A., Smith, D.B. and Warren, S.C. 1978. Seasonal variations of tritium and other constituents of groundwater in the Chalk near Brighton, England. J. Inst. Water Engr. Sci. 32, 123.

237. Foster, S.S.D. 1975. The Chalk groundwater tritium anomaly - a possible explanation. J. Hydrol. 25, 159.

238. Price, M., Bird, M.J. and Foster, S.D.D. 1976. Chalk pore-size measurements and their significance. Water Serv. 80, 596.

239. Smith, D.B., Downing, R.A., Monkhouse, R.A., Otlet, R.L. and Pearson, F.J. 1976. The age of groundwater in the Chalk of the London Basin. Water Res. Res. 12, 392.

240. Downing, R.A., Pearson, F.J. and Smith, D.B. 1979. The flow mechanism in the Chalk based on radioisotope analyses of groundwater in the London Basin . J. Hydrol. 40, 67.

241. Bath, A.H. and Edmunds, W.M. 1981. Identification of connate water in interstitial solution of Chalk sediment. Geochim. Cosmochim. Acta. 45, 1449.

242. Coope, G.R. 1977. Fossil Coleopteran assemblages as sensitive indicators of climate changes during the Devensian (last) cold stage. Phil. Trans. R. Soc. Lond. Ser. B. 280, 313.

243. Lamb, H.H., Lewis, R.P.W. and Woodroffe, A. 1966. Atmosphere circulation and main climatic variables between 8000 to OBC. pp174-215 Royal Meteorological Society, London.

244. Owen, M., Connorton, B.J. and Robinson, V.K. 1977. The hydrogeology of the Thames Groundwater Scheme. Mem. Int. Ass. Hydrogeologists. Birmingham XIII, D20-31.

245. Frissel, M.J. and Van Veen, J.A. 1982. A review of models for investigating the behaviour of nitrogen in Soil. Phil. Trans. R. Soc. Lond. Ser. B. 296, 341.

246. Tomlinson, T.E. 1970. Trends in nitrate concentrations in English rivers in relation to fertilizer use. Water Treat. Exam. 19, 277.

247. Reeves, M.J. 1977. A procedure for the prediction of nitrate levels in water supplies in the United Kingdom. Prog. Wat. Tech. 8, 161.

248. Spears, D.A. 1979. Porewater composition in the unsaturated zone of the Chalk with particular reference to nitrates. Q.J.Eng. Geol. Lond. 12, 97.

249. Young, C.P. and Morgan-Jones, M. 1980. A hydrogeochemical survey of the Chalk groundwater of the Banstead area, Surrey, with particular reference to nitrate. J. Inst. Wat. Eng. Sci. 34, 213.

250. Foster, S.S.D., Cripps, A.C., Smith-Carington, A. 1982. Nitrate leaching to groundwater. Phil Trans. R. Soc. Lond. 296, 477.

251. Foster, S.S.D. and Smith-Carington, A. 1980. The interpretation of tritium in the Chalk unsaturated zone. J. Hydrol. 46, 343.

252. Barker, J.A. and Foster, S.S.D. 1981. A diffusion exchange model for solute movement in fissured porous rock. Q.J. Eng. Geol. Lond. 14, 17.

253. Lindsay, W.L., Sadiq, M. and Porter, L.K. 1981. Thermodynamics of inorganic nitrogen transformations. Soil Sci. Soc. Am. J. 45, 61.

254. Whitelaw, K. and Edwards, R.A. 1980. Carbohydrates in the unsaturated zone of the Chalk, England. Chemical Geology. 29, 281.

255. Painter, H.A. 1970. A review of literature on inorganic nitrogen metabolism in microorganisms. Water Research. 4, 393.

256. Jannasch, H.W. 1960. Versuche uber Denitrifikation und die ver fugbarkeit des Sauerstoffes in Wasser und Schlamm. Arch. Hydrobiol. 56, 355.

257. Chang, J.P. and Morris, J.G. 1962. Studies on the utilization of nitrate by Micrococcus denitrificans. J. Gen. Microbiol. 29, 301.

258. Pichinoty, F. and D'Ornano, L. 1961. Sur le mécanisme de l'inhibition par l'oxygene de la denitrification bacterienne. Biochim. Biophys. Acta. 52, 386.

259. Bergersen, F.J. 1977. Physiological chemistry of nitrogen fixation by legumes p519-555. In Hardy, R.W.F. and Silver, W.S. (Ed.) A treatise on denitrogen fixation, Sec III. John Wiley and Sons Inc., New York.

260. Standford, G., Legg, J.O., Dzienia, S. and Simpson Jr, E.C. 1975. Denitrific and associated nitrogen transformations in soil. Soil Sci. 120, 147.

261. Andrews, J.N. and Kay, R.L.F. 1982. $^{234}U/^{238}U$ activity ratio of dissolved uranium in groundwaters from a Jurassic limestone aquifer in England. Earth, Planet. Sci. Let. 57, 139.

262. Bath, A.H., Edmunds, W.M., Andrews, J.N. 1979. Palaeoclimatic trends deduced from the hydrochemistry of a Triassic sandstone aquifer, United Kingdom. in Isotope Hydrology Vol II, p545-568. Proc. Sym. Neuherberg, Joint I.A.E.A. and U.N.E.S.C.O. 1978. Pub. I.A.E.A., Vienna.

263. Berner, R.A. 1980. Early Diagenesis, a theoretical approach. Princeton Series in Geochemistry. Princeton Univ. Press, Princeton, New Jersey, U.S.A. pp241.

264. Rolston, D.E., Fried, M. and Goldhammer, D.A. 1976. Denitrification measured directly from nitrogen and nitrous oxide gas fluxes. Soil Sci. Soc. Am. J. 40, 259.

265. Central Water Planning Unit. 1977. Nitrate and water resources with particular reference to groundwater. C.W.P.U. Reading Bridge House, Reading. pp64.

266 Dowdell, R.J. 1982. The fate of nitrogen applied to agricultural croips with particular reference to denitrification. Phil. Trans. R. Soc. Lond. B. 296, 363.